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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE IMC/PRAYON URANIUM RECOVERY PROCESS

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INTRODUCTION

Phosphoric acid is a basic product produced around the world. Phosphate rock is mixed with sulfuric acid to produce phosphoric acid and gypsum. The phosphoric acid is sold as merchant acid or is further processed to produce various fertilizers and/or animal feed products.

Acid produced in Central Florida generally contains about 140 - 180 parts per million of uranium, equivalent to approximately 0.5 to 0.6 kg U₃O₈ per MT P₂O₅. U₃O₈ contains 84.8% uranium.

By 1982 the U. S. production capacity for extracting uranium from wet-process acid using Florida rock phosphate as acid feed stock will be about 5 million annual pounds or 2500 short tons as U₃O₈.

IMC through its New Wales complex in Florida and satellite modules at two neighboring plants will account for about 43% of the stated production capacity.

In the period 1957 - 58, IMC operated a uranium extraction plant at its Bonnie complex. The process used pyrophosphate esters as the extractant of tetravalent uranium from 26 - 30% P₂O₅ acid. Over the life of the project, uranium recovery increased from 50% to 75% of that present in the feed acid. Competition from western producers of high grade uranium ores made the process uneconomic and the Bonnie operation was closed.

The above process (Figure 1)⁽¹⁾ had two severe disadvantages:

1. Recoveries were low.
2. It recovered uranium in the tetravalent state (U⁺⁴). Over 80% of the uranium in phosphate rock is in the hexavalent (U⁺⁶) state. The proportion of hexavalent uranium increases during attack with sulfuric acid. Using the pyrophosphate tetravalent process required reducing the uranium in the entire acid stream. Reduction is accomplished by adding metallic iron to the acid. As the Fe⁺³ content of the acid is replaced by Fe⁺², the U⁺⁶ reduces to U⁺⁴. Adding iron adds an undesirable impurity to the phosphoric acid, especially when the entire acid stream must be reduced. In the Bonnie operation the high iron content of the raffinate resulted in increased use of acid P₂O₅ per ton TSP to yield a sticky product.

In 1974 - 76 there was a six-fold increase in the price of yellowcake. Uranium extraction from wet-process acid appeared economically attractive under the new price structure. (Figure 2)⁽²⁾

Disillusioned with its earlier experience of extracting uranium in the tetravalent state, IMC opted for the Oak Ridge National Laboratory's DEHPA-TOPO process, that extracts hexavalent uranium from filter acid, as the choice for re-entry into the field.

Although Oak Ridge⁽³⁾ had indicated that a new process, OPAP, a mixture of

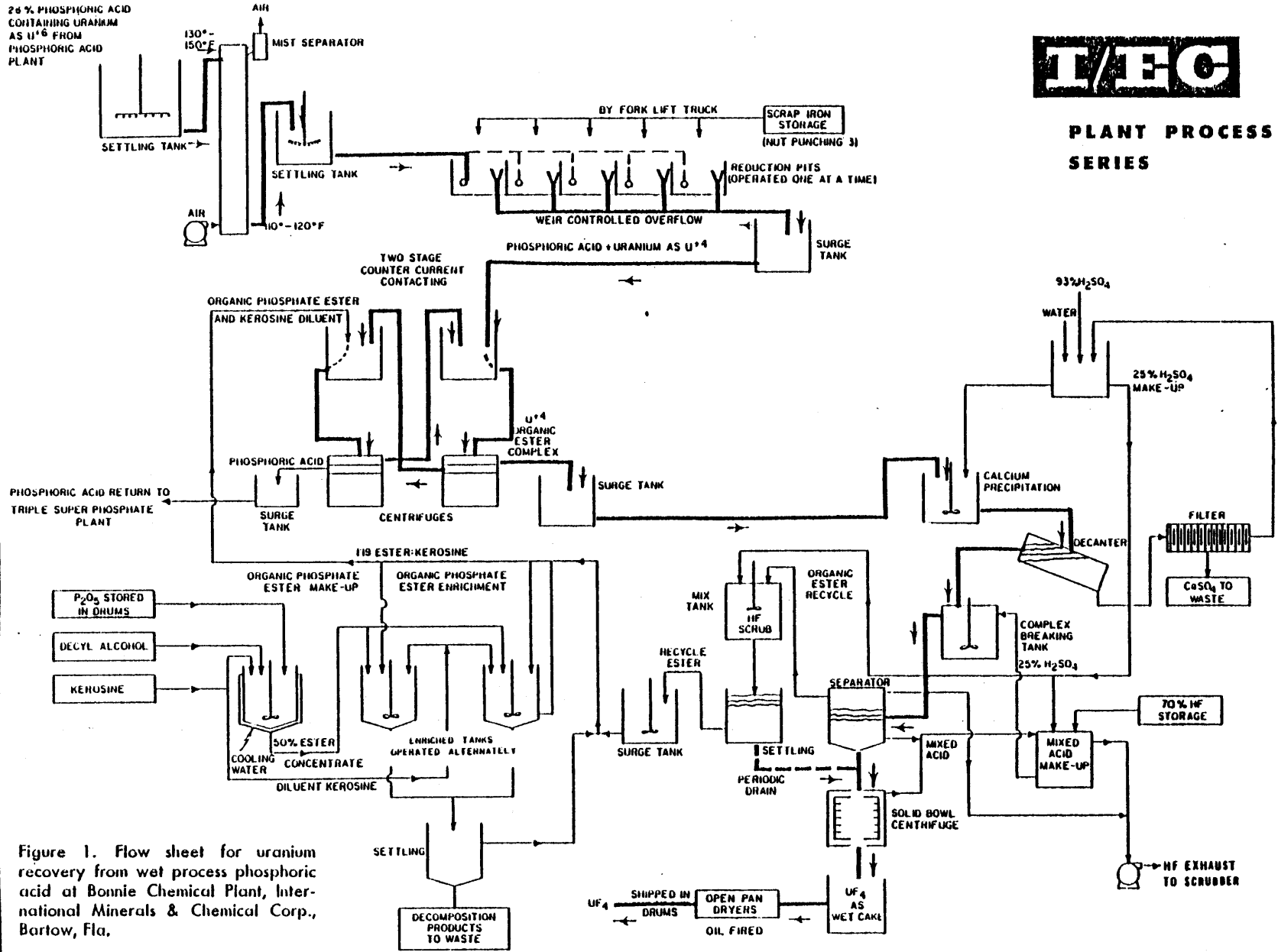


Figure 1. Flow sheet for uranium recovery from wet process phosphoric acid at Bonnie Chemical Plant, International Minerals & Chemical Corp., Bartow, Fla.

FIGURE 1

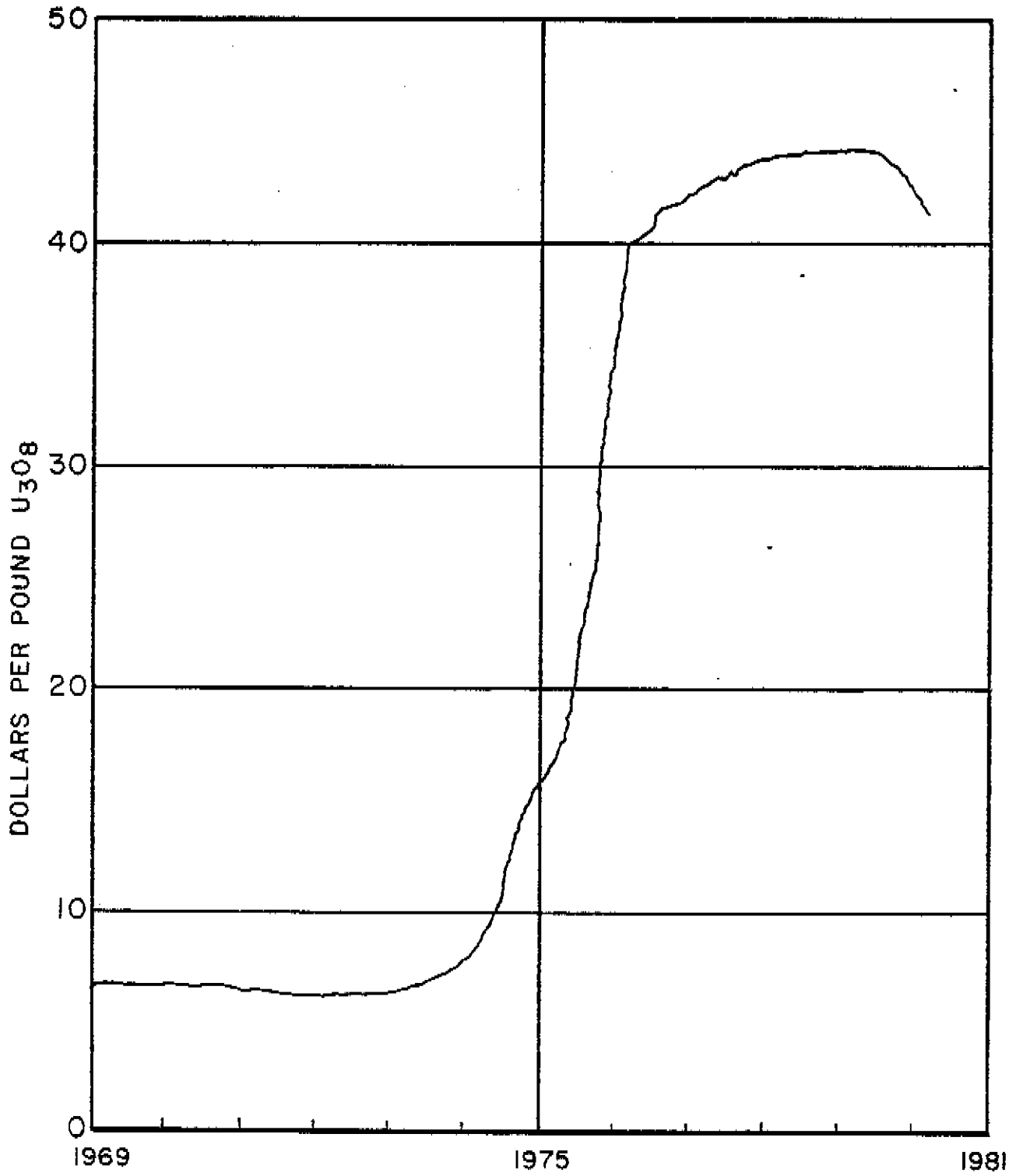


FIGURE 2

mono and dioctylphenyl phosphoric acids could provide substantial investment savings due to the high extraction coefficients found in the OPAP process, the OPAP process had three severe disadvantages:

1. It extracted tetravalent uranium, requiring reduction of the entire acid stream by the addition of metallic iron.
2. It required 54% P₂O₅ acid in the primary stripping section. The strip acid was diluted before second cycle extraction which increased the evaporation load in the main plant.
3. The OPAP organic solvent was not stable.

In the DEHPA-TOPO process there are two levels of uranium valence.

In the first level, the entire acid stream is oxidized to yield hexavalent uranium before primary extraction with a DEHPA-TOPO organic solvent.

The uranium is stripped from the primary organic solvent with a reduced phosphoric acid stream. The stripping operation requires a tetravalent uranium for transfer from the organic into the strip acid. However, the stripping operation is also a concentration operation whereby the concentration of uranium in the process liquors is increased by a factor of about sixty (60).

Therefore, the strip acid is only one-sixtieth (1/60) of the volume of primary acid. This means that only 1.5% of the amount of iron must be added to the system as compared to what would be needed if the entire primary acid stream had to be reduced.

When IMC first decided to re-enter the field of recovering uranium from wet process acid it had intended tentatively to be involved in providing only a satellite module at New Wales from where concentrated strip acid would be shipped to a central refinery where the second cycle stripping and final processing step would take place. The central refinery, a separate corporation, had plans to start up a satellite module at a competitor's plant, and when that was on stream proceed with the New Wales satellite module.

After two years of waiting for the first module to reach capacity, IMC decided to re-enter the field on its own from primary extraction through final processing of yellowcake.

Enough had been learned about the first module and the refinery problems to realize that the major operating problem was due to the organic content of the black acid.⁽⁴⁾ If a satisfactory precleaning step could be devised, it was felt that there was enough information available from the Oak Ridge literature to scale up the remainder of the process with a minimum of bench and pilot plant work.

CREATION OF THE JOINT IMC/PRAYON CONCEPT

International Minerals & Chemical Corporation began development work on their uranium recovery process in early 1977. The process developed is now in operation at IMC's New Wales complex and portions of the process (primary modules) have been installed at CF Industry's Bartow and Zephyrhills facilities. Concurrent with IMC's development work, Societe de Prayon and Metallurgie Hoboken-Overpelt, two Belgium concerns, were developing technology for the recovery of uranium from phosphoric acid produced in Belgium. A facility was being installed in the Prayon plant in Belgium. Technology joint venture negotiations began and it was determined that a combination of the technologies and experience of all parties would result in a process package applicable to a wide range of wet process phosphoric acids.

These combined technologies and the breadth of experience possessed by the companies allow this technology to be applied to phosphoric acids ranging from Florida material; which, as is known, is extremely dark in color and contains substantial quantities of humates; to low color acid such as those made from North African rock; that is lower humic levels and lighter in color.

The process is based on the two-cycle Oak Ridge National Laboratory Reductive Strip System and has been modified to allow for the variations in phosphoric acid production techniques around the world. A key feature of the IMC/Prayon process is the use of extensive phosphoric acid clarification and pretreatment using activated carbon. In the case of Florida phosphoric acid, the resulting clean material is green, solids free and limits the formation of emulsions in the solvent extraction process.

A second key feature is the technique employed to precipitate uranium. In the plant operating in Central Florida, uranyl peroxide, of exceptional purity, is produced. Modifications to the conventional uranyl peroxide precipitation technique have allowed the incorporation of this step into the process, thus minimizing the potential for metallic contamination.

In addition, the uranium-free, clean, green acid which is returned to the phosphoric acid facility, results in certain processing benefits to the existing phosphoric acid plant.

The basic IMC/Prayon uranium recovery process involves several specific stages. Figure 3 shows a block diagram which will be used as a reference to describe the process currently in use at New Wales.

As a result, this discussion is concerned with Florida phosphoric acid since, in most cases, this is the most difficult material to work with. Florida acid contains a substantial amount of humic material and, for the most part, is produced from uncalcined rock.

PROCESS SUMMARY

Referring to Figure 3, acid is received as primary or "number one" filtrate from the existing phosphoric acid facility, and is stored in surge tanks. The acid is then cooled, utilizing spiral heat exchangers, pretreated, clarified, then passed through activated carbon columns. This entire system is referred to as the "Acid Clean-Up" operation. It is in this step that the solids and humic materials are removed from the acid to produce a clean, green phosphoric material.

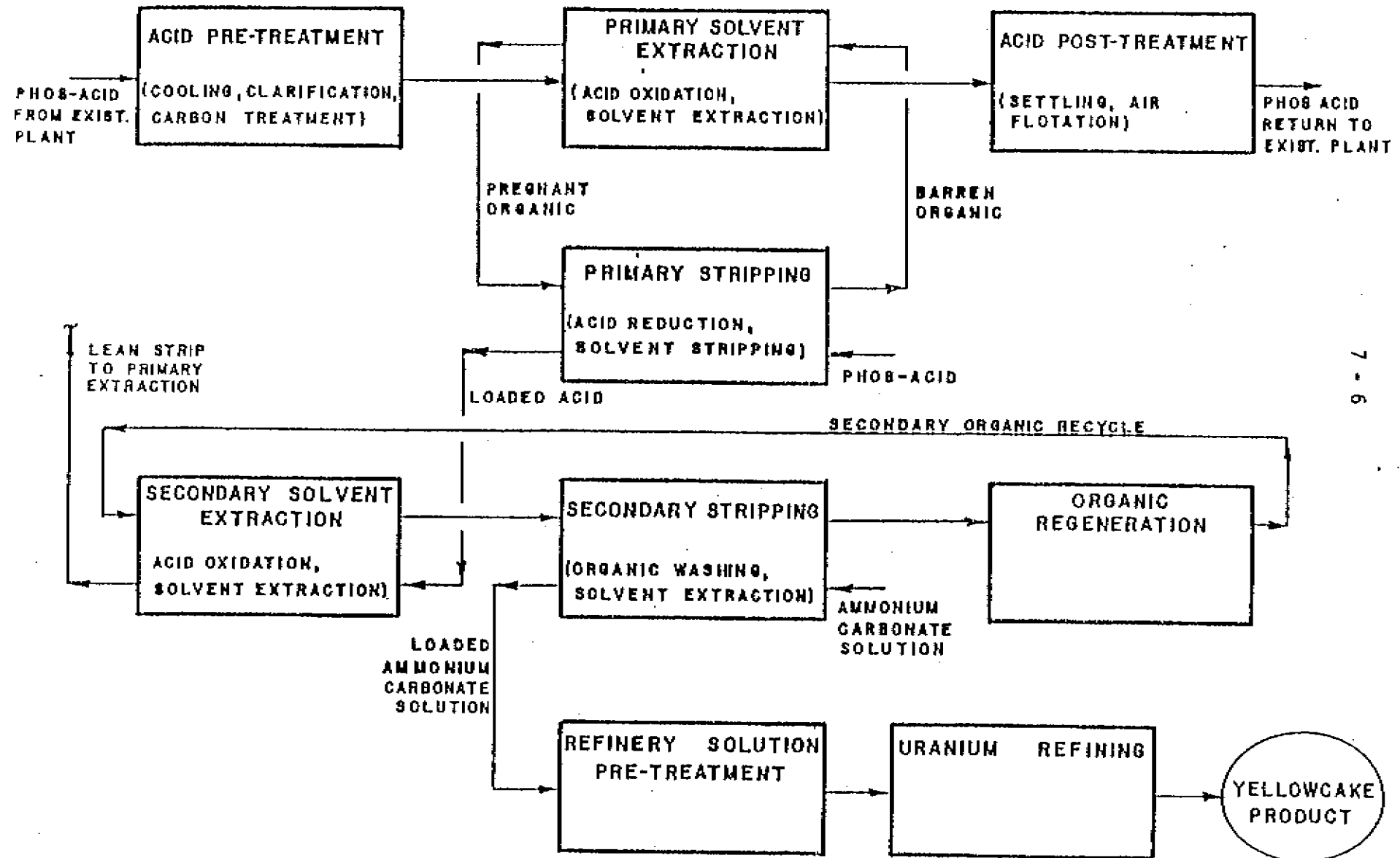
The acid then enters the Primary Solvent Extraction System. The first phase of this operation involves oxidation of the acid in order to convert all of the ferrous iron to the ferric state. This insures that the uranium is present in the +6 valence state.

Following the oxidation step, the acid is contacted with DEHPA-TOPO (di-2-ethyl hexyl phosphoric acid and tri-N-octyl phosphine oxide in a kerosene type diluent) in a solvent extraction mixer-settler system modified to accommodate phosphoric acid. A counter-current contacting technique is utilized.

Pregnant organic is then contacted with a small stream of phosphoric acid which has been reduced with iron metal. Uranium transfers from the pregnant organic to the reduced acid. A substantial concentration increase (up to 60 times) is accomplished utilizing this technique, which is based on work conducted by the Oak Ridge National Laboratory.

IMC/PRAYON URANIUM RECOVERY PROCESS

OVERALL BLOCK DIAGRAM



Raffinate phosphoric acid, leaving the Primary Extraction Circuit, is then treated to remove any entrained organic and returned to the phosphoric acid plant. Treatment consists of a settling step, followed by air flotation.

The loaded strip acid is again oxidized and treated in a Secondary Extraction Circuit with DEHPA-TOPO. The operation is the same as in the primary circuit. However, the volumes involved are considerably smaller because of the higher concentration of uranium in the strip acid. The lean strip, minus most of its uranium content as it exits the Secondary Extraction Circuit, is returned to the feed end of the Primary Circuit.

Secondary pregnant organic is first washed with water to remove any entrained P_2O_5 , then stripped with a solution of ammonium carbonate. The DEHPA is converted to the ammonium form and the uranium transfers to the carbonate solution. Barren organic is regenerated, by acidifying the DEHPA and returned to the Secondary Extraction System.

The secondary loaded strip solution, containing the ammonium carbonate-uranium complex, is prepared for uranium precipitation in a proprietary pretreatment technique. The prepared solution is pumped to the Refinery Circuit.

In the Refinery, uranium is precipitated from the prepared secondary strip solution as uranyl peroxide. This material is exceptionally pure and precipitates easily. The precipitated peroxide is thickened, washed, centrifuged, then dried in a multiple hearth-type dryer. It is not necessary to calcine this material due to its purity. Over 95% of the uranium extracted from the primary acid stream is recovered as yellowcake.

DETAILED DISCUSSION

The following will describe some of the individual process steps in more detail. It will review also known areas of wet-phosphoric acid technology that affect general process areas in the uranium recovery plant.

Acid Cooling and Pretreatment

A simplified diagram of the Acid Cooling and Clean-Up System is shown in Figure 4.

Phosphoric acid received from the existing P_2O_5 facility as filtrate product, is first cooled. Evaporative or air cooling could have been used. At the New Wales facility however, spiral heat exchangers (coolers) have been utilized quite successfully. As is common in USA phosphoric acid plants, all the process effluents recirculate through a pond area. Pond effluent is used to slurry the gypsum which settles in one section of the pond area. Another section of pond is used to lower the temperature of the pond water by surface evaporation. In Florida, the pond effluent or pond water has a temperature of $27^\circ - 35^\circ C$. It is an effective medium for cooling the attack filtrate down to $49^\circ C$. The latter temperature has been found to be optimum in order to increase the extraction coefficient, to minimize diluent evaporation, and to precipitate additional solids from the acid. A schematic of the spiral cooler is shown in Figure 5.

Periodically, the unit is "rotated", i.e., the acid flow is transferred to the water side and vice versa.

Phosphoric acid is a high scaling material and post-precipitation of solids presents a major design problem. Design of any commercial installation must consider these important aspects.

IMC/PRAYON URANIUM RECOVERY PROCESS

ACID COOLING AND PRE-TREATMENT

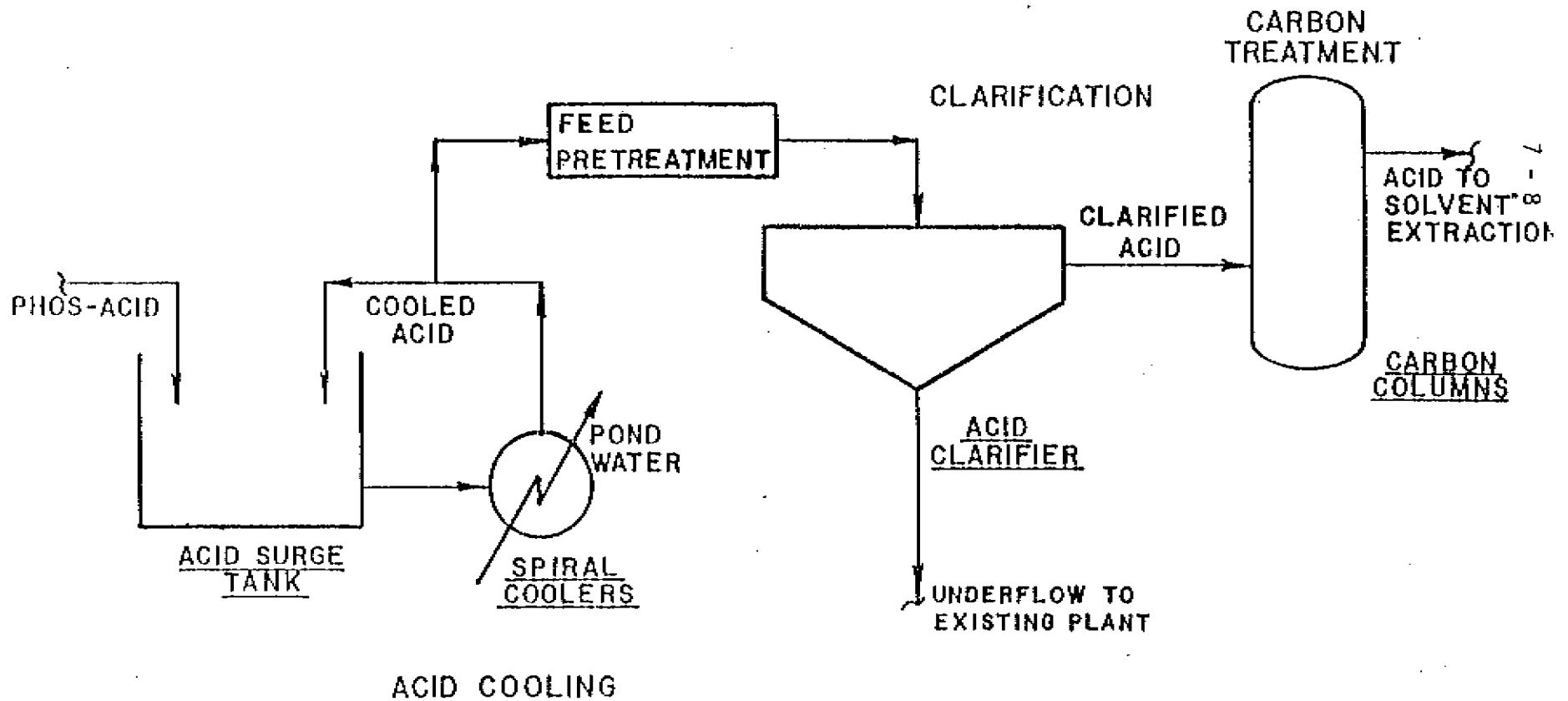
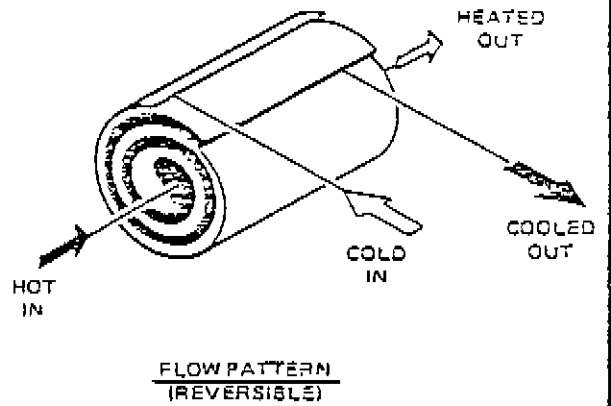
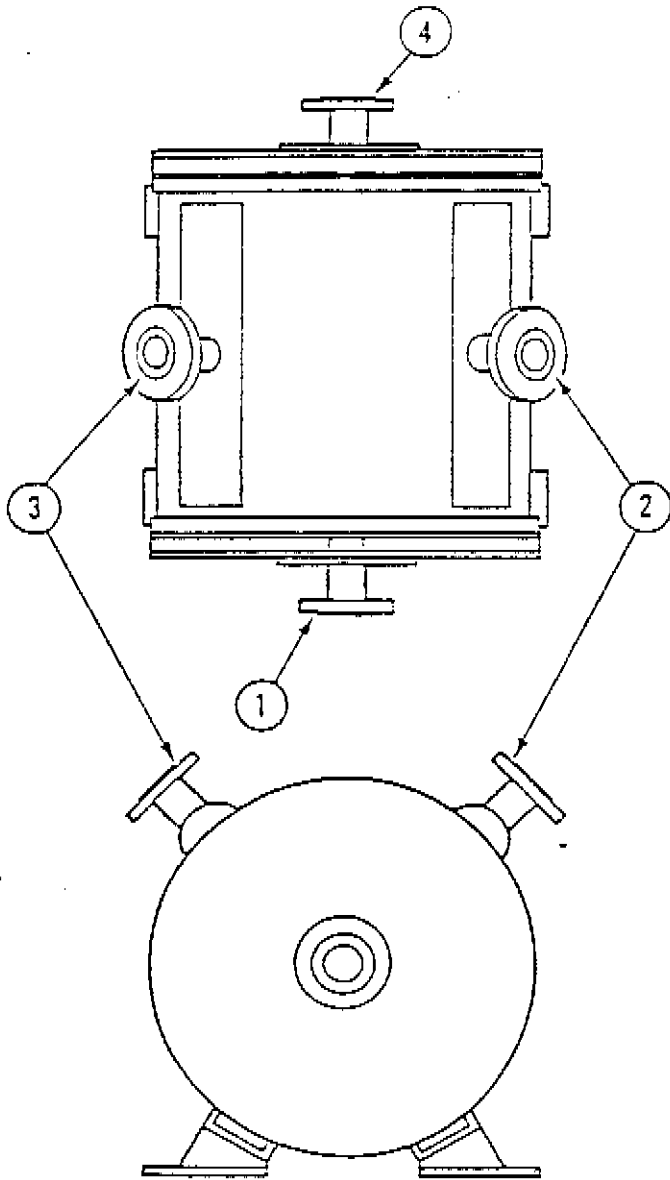


FIGURE 4



NOZZLES CONNECTIONS	NO. REC'D.	SIZE
1. HOT IN	1	8" DIA.
2. COOLED OUT	1	8" DIA.
3. COLD IN	1	8" DIA.
4. HEATED OUT	1	8" DIA.



URANIUM RECOVERY FACILITY
 AT NEW WALES CHEMICALS, INC.
 MULBERRY, FLORIDA

ACID SPIRAL COOLER
 EQUIP. NO. 10-38201 A & B,
 10-28302 A & B

FIGURE 5

The spiral cooler units have proven to be extremely effective for use in 30% acid cooling. Under normal conditions, the coolers are rotated every twenty-four hours. After rotation of the coolers, when acidic pond water is being circulated through the previous acid section, the acidic water removes any scale precipitated before the rotation.

Maintenance on the units has been minimal. It is imperative that the valves of the unit be programmed to minimize dilution of acid by pond water and loss of acid to pond water during the rotation sequence.

The cooled acid enters the clarifier feed pretreatment section. It should be pointed out that one of the most important process steps in the IMC/Prayon system is the use of extensive acid clean up in order to minimize crud formation and phase separation problems in the Solvent Extraction Circuit.

The severity of crud formation and phase separation problems in the organic extraction phase of the process has jeopardized other systems trying to extract uranium from wet process phosphoric acid. The desire for a solids and organic free acid feed to the solvent system led to the use of special techniques involving clarification and the use of activated carbon adsorption in the New Wales plant.

The combination of cooling and clarification results in an acid with a 0.1 v/v solids content as determined by centrifuging a sample for 10 minutes at 2000 RPM.

Humic material from the phosphoric acid is adsorbed by the carbon, resulting in a green acid product. The black color of wet process acid is due to a number of organic compounds (aliphatic hydro-carbons and fatty acids plus porphyrin type compounds) labelled generally as "humic acid", or humates.⁽⁵⁾ The plant personnel label the organic content as "color".

Color is determined on a centrifuged sample of acid using a spectrophotometer set at 408 nm to measure absorbance. The 408 wavelength has been shown to be one that varies linearly as a sample is diluted. Filter acid varies from a color of about 2 when dried rock is fed to the attack system, to colors in the 3 to 5 range when wet-grinding is used to process attack feed.

Clarification removes 30% to 50% of the color. The activated carbon removes color to the desired range of 0.2 to 0.6.

That activated carbon can be used to remove humates is well known and standard procedures are available for carbon evaluation and applicability.^(6, 7, 8, 9, 10) The key to the process in use at New Wales, however, is the economical use of carbon and the basic design required to accommodate phosphoric acid.

A major portion of the IMC development program was devoted to the activated carbon adsorption and regeneration system. Economics dictate that carbon must be reused many times before it is discarded. To date, the plant has been pleased with the operation of the carbon column system. The carbon does lose some surface area after several regenerations and the amount of carbon required to treat a given quantity of phosphoric acid increases.

It has been observed, however, that once the initial "run in" has been completed, typically five to ten cycles, the rate of surface area loss decreases, and the surface area of carbon appears to reach steady-state. Carbon usage, per unit of P₂O₅, also tends to stabilize.

A cycle is the period that a carbon column is in the downstream product position through its transfer to the upstream feed position and regeneration.

Figure 6 shows the carbon surface area as a function of number of regenerations. During the initial regenerations, a fairly rapid decrease in surface area is noted. The decrease diminishes with an increase in the number of regenerations. The amount of surface available with this particular type of carbon, even after twenty-five regenerations, is more than acceptable for economic use in the Acid Clean-Up System.

Figure 7 shows the carbon utilization as a function of the number of carbon column regenerations. The definition of carbon utilization is the weight of carbon utilized per unit weight of phosphoric acid solution, and is expressed as percent by weight of acid.

After the first several regenerations, carbon utilization reaches a fairly steady value. It is important to note that the utilization rate is not the same as carbon make-up. The latter is the amount of new carbon which must be added due to the various carbon losses. Carbon utilization on the other hand, is the amount of material which must be regenerated after treating a given amount of phosphoric acid.

Obviously, one of the key parameters in this operation is the chemical regeneration technique. It is desirable to have carbon which can be utilized for a number of cycles and which maintains its adsorptive capacity throughout its useful life. Figure 8 compares product column breakthrough curves for new carbon, (material that has had less than five regenerations) with used carbon, (material with more than twenty regenerations).

Under normal conditions, the columns are rotated at forty hours. Columns are rotated when the carbon column product reaches a color of 0.6 or 40 hours, whichever comes first. The feed column is removed from service for regeneration, and a fresh regenerated, column is placed in the product position. The other columns move upstream. The complicated valving during rotation is handled by an automatic computer.

Comparing the product acid colors during the forty-hour run, it is seen that the used material has maintained a high degree of its original adsorptive capacity. For reference purposes, an acid color of 0.5 would be a bright green material. Normal black Florida acid usually has an acid color of 3 - 4, on this particular scale, since New Wales began to use wet-grinding.

To date, the carbon column system has worked well and it is felt that it provides an effective means of pretreating the acid prior to solvent extraction.

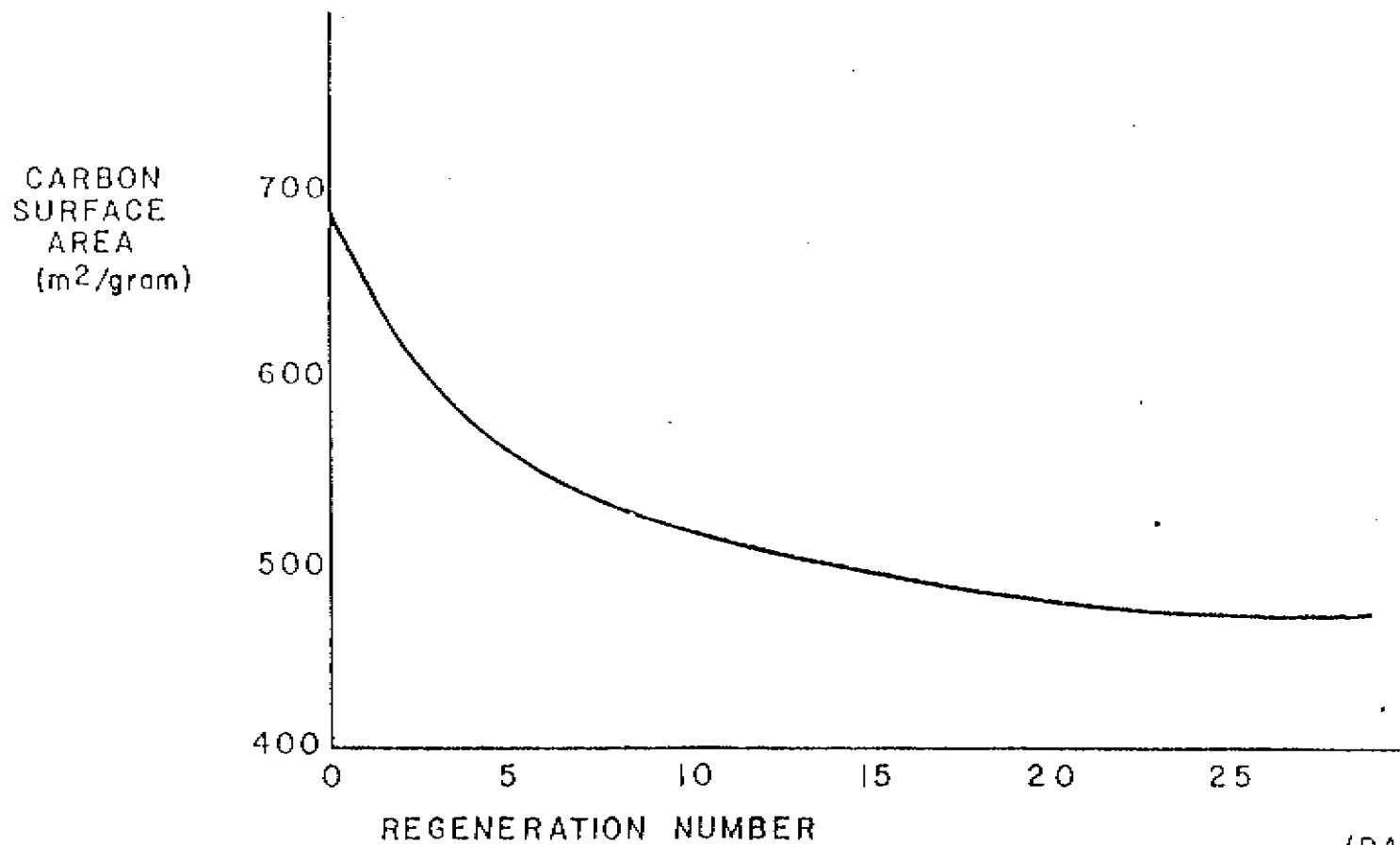
The cleaned acid is then transferred to the solvent extraction area. Figure 9 presents a breakdown of the Oxidation, Extraction, Stripping and Acid Post-Treatment steps. Design U_3O_8 concentrations are shown for the primary streams.

Acid Oxidation

In the oxidation step, the valence of the uranium is adjusted using an oxidizer. For DEHPA-TOPO to be an effective extractant, the uranium must exist in the U^{+6} valence state. Due to the iron-uranium redox couple, it is essential that all iron present in the phosphoric acid, at this point, be in the Fe^{+3} state.

Many techniques are available to accomplish oxidation. For example, air, oxygen, hydrogen peroxide, etc. At New Wales hydrogen peroxide is being used for the initial operation due to the ease of operation, and simple equipment design. However, a continuing program is underway to develop alternate techniques.

CARBON SURFACE AREA AS FUNCTION OF NUMBER OF REGENERATIONS



(DATA FROM COLUMN A-2)

FIGURE 6

CARBON UTILIZATION AS FUNCTION OF NUMBER OF REGENERATIONS

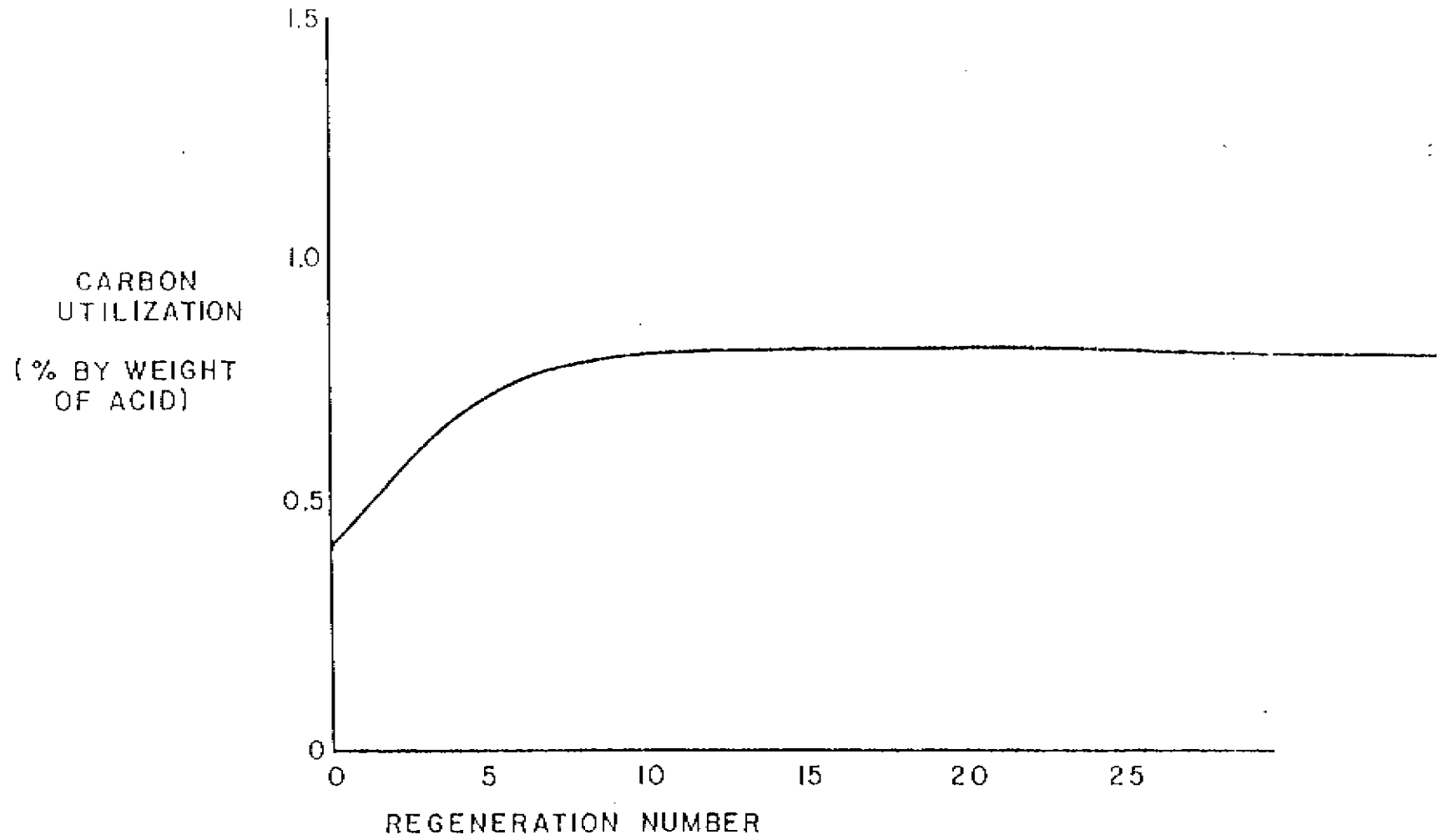


FIGURE 7

PRODUCT COLUMN BREAKTHROUGH CURVES

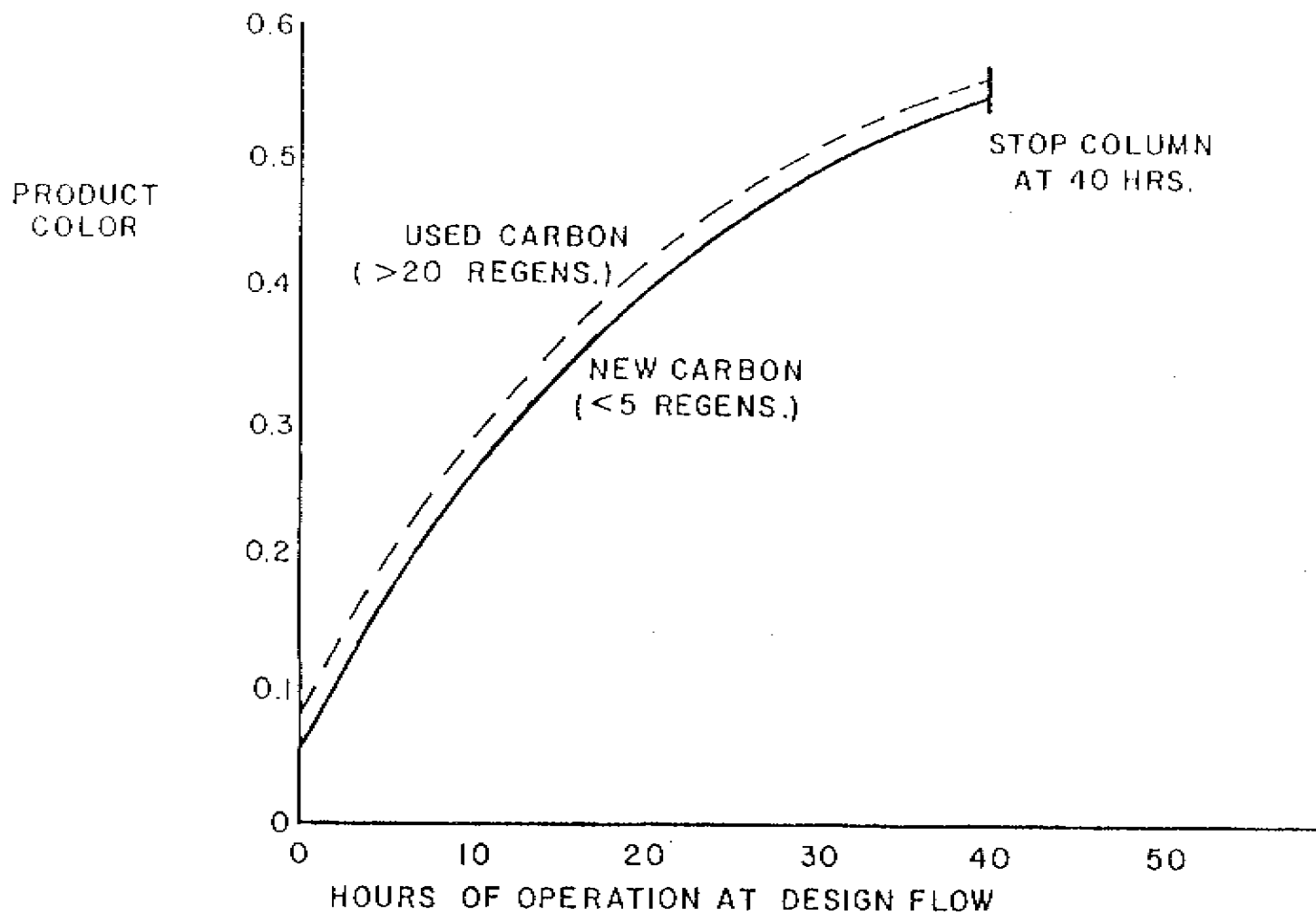


FIGURE 8

IMC/PRAYON URANIUM RECOVERY PROCESS

ACID OXIDATION, PRIMARY SOLVENT EXTRACTION/ STRIP AND ACID POST TREATMENT

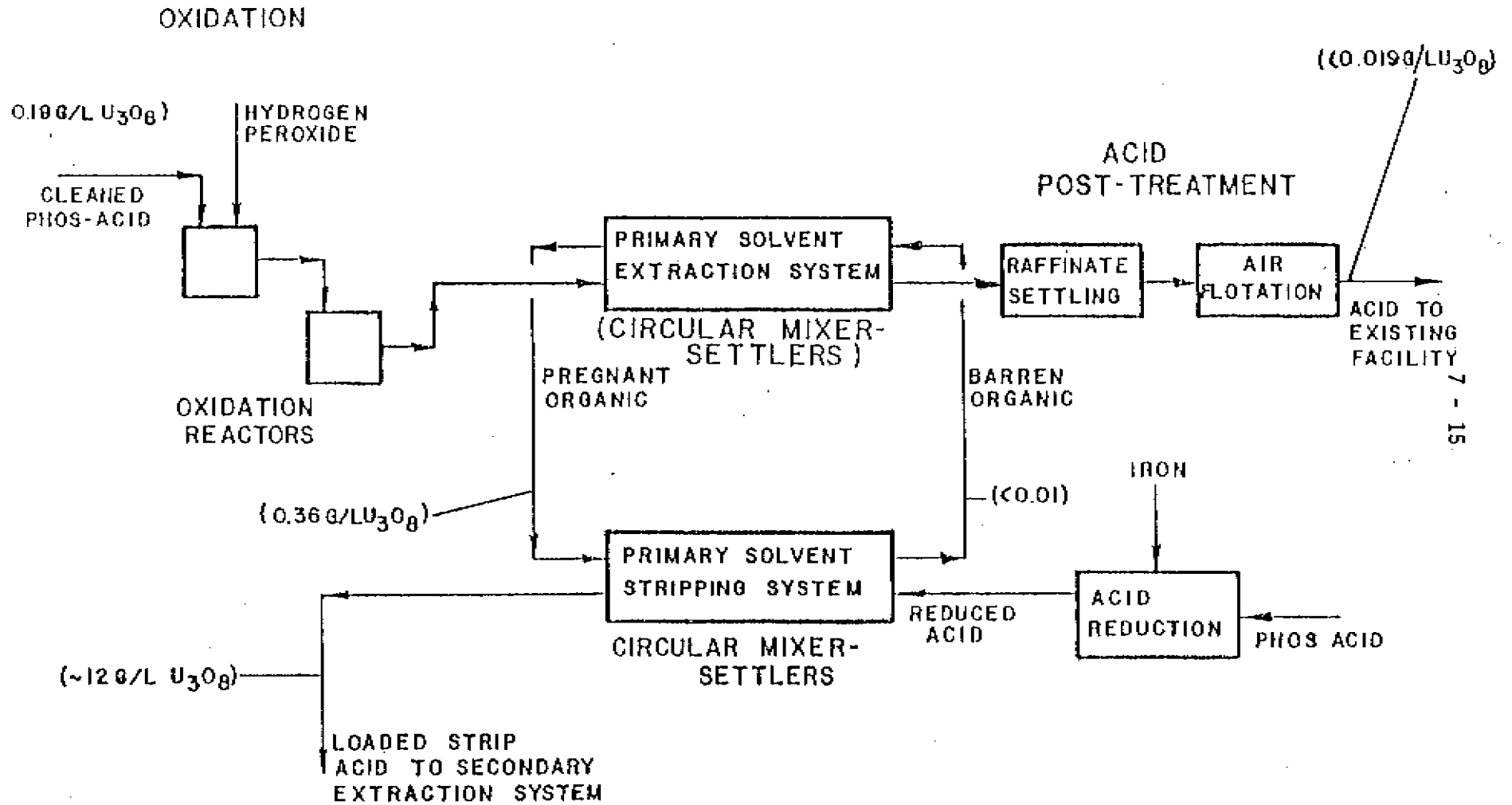


FIGURE 9

It is well known that many chemical oxidants are available, many of which are less expensive than hydrogen peroxide. However, if phosphoric acid is to be used to produce chemicals, or to be sold as merchant acid, it is extremely important that contamination of the acid by additives be minimized as much as possible.

Thus, an oxidizer, such as sodium chlorate, is not an acceptable alternative because the chlorine causes corrosion of stainless steel equipment. Nitric acid, while producing acceptable oxidation, adds nitrates to the acid, an undesirable additive to chemicals and feed ingredients.

It should be pointed out here that New Wales receives rock varying from day to day between 66 to 68 BPL. The rock is delivered by rail or truck from four IMC mines, each mine having its own peculiar makeup of accessory minerals. The Fe^{+3} and Fe^{+2} levels vary not only from mine to mine, but within each mine from area to area.

The amount of oxidizer required can vary substantially from day to day depending on the rock source and the operating conditions of the phosphoric acid attack circuit. The Fe^{+2} level is monitored continually to optimize oxidizer usage.

Primary Solvent Extraction and Strip

Oxidized phosphoric acid is contacted with a mixture of DEHPA-TOPO, dissolved in a diluent, utilizing a counter-current solvent extraction technique. At New Wales, four stages of extraction are employed. More or less stages can be used depending on specific process requirements.

The DEHPA-TOPO concentration is normally 0.5 Molar DEHPA and 0.125 Molar TOPO. The overall system, as indicated previously, is based on work conducted at Oak Ridge National Laboratories. (11, 12, 13, 14)

The contacting of an aqueous and organic system is a fairly standard practice in a number of metallurgical recovery operations. In a similar manner, phosphoric acid and organic contacting can be accomplished in fairly conventional equipment if the peculiar behavior of wet acid is incorporated into the design of the plant equipment. Unfortunately, even though the phosphoric acid has been cooled, clarified, etc., it still has a tendency to scale and post precipitate to some extent. This tendency must be recognized during design of the overall process package.

Rectangular pumper mixers and/or circular mixer-settler units can be employed for the contacting steps. At New Wales and at the CF Modules, circular mixer-settlers, utilizing gravity flow for the phosphoric acid, are employed. This design was chosen due to the size of the flows involved (4000 - 5000 liters/minute) as the most conservative approach at the time.

In the system, aqueous (acid) to organic volumetric ratio is maintained normally at about 2:1 in all but the last mixer-settler unit. The last unit is typically operated organic continuous in order to minimize organic entrainment in the acid.

The low uranium acid (raffinate) exiting the last mixer-settler enters the Acid Post-Treatment System, to be described later. The data in Figure 9 indicate a 90% minimum extraction of the uranium in the feed acid.

Pregnant organic is stripped with a small stream of reduced phosphoric acid. The strip acid is about 1.5 percent of the main acid stream on a volume basis. Reduction is effected by adding iron metal to provide the proper amount of Fe^{+2} in the system.

Since DEHPA-TOPO has little affinity for U^{+4} , the presence of Fe^{+2} in the strip acid reverses the extraction reaction. The stripping of the organic is efficient and produces a substantial increase in uranium concentration. Usually, a 55 - 65 fold increase in U concentration is observed in the strip acid, compared to the main phosphoric acid stream. Therefore, the loaded strip acid will contain about 10 - 12 g/L of U_3O_8 .

The stripping operation is extremely critical if high recoveries are to be achieved. If uranium is not removed effectively from the organic, the barren organic, returning to the Primary Extraction Cycle with a certain load of uranium, has less potential for removing more uranium from the phosphoric acid. This results in lower uranium extraction efficiencies and recoveries.

Since stripping is such a critical step, several techniques are employed in the IMC/Prayon System to insure proper Fe^{+2} concentration but the most important factor is close watch of the system to obtain steady operation. Despite the large hold-up in the extraction and stripping mixer-settler circuit, the dynamic response of the system can be deceiving because there is little surge between the individual mixer-settlers. For example, an additional hundred gallons of acid material pumped into a mixer causes a ripple of liquid throughout the circuit. For this reason, changes in operating parameters must be made in a slow, deliberate fashion.

Figure 10 shows a view of the Primary Solvent Extraction Area. The large circular vessels are the solvent extraction settlers.

As indicated in the earlier discussion on acid clean-up, a basic consideration has been to minimize solvent extraction related problems by going to extreme lengths in the pretreatment system to remove potential crud forming materials. This has been accomplished by the use of the clarification and activated carbon adsorption system.

Removal of humates (color) results in a significant decrease in the amount of "crud" formed in the Solvent Extraction circuit. Humic material and other inorganic and organic contaminants can transfer from the acid to the organic phase. In some cases, they will precipitate in the organic phase and accumulate at the liquid-liquid interface in the settler.

Small amounts of crud do not appear to interfere to any appreciable extent with the solvent extraction operation. Large amounts, however, can produce severe problems. The goal in the IMC/Prayon Process has been to minimize the potential for crud formation problems.

Figure 11 shows the impact of acid clean-up on crud formation. The amount of crud is shown as a function of acid color.

As indicated earlier, green phosphoric acid produced in the clean-up system, has color of about 0.2 to 0.6. Black phosphoric acid, from the filters will generally have a color of 3 to 4. Clarified acid normally has a color in the range of 1.2 to 1.8. The rate of crud formation is definitely not linear and once a given threshold is reached, the amount of crud formed increases significantly with an increase in acid color.

Higher humic acids (beer color) can be handled in a solvent extraction circuit if proper processing techniques are employed. Indeed, there are other uranium recovery from phosphoric acid facilities operating with brown acid. The clean-up systems employed in these processes remove some humic material and a majority of the inorganic solids from the acid. However, the pretreated acid leaving the circuits still has soluble humates present. Some of the humates may transfer to the organic phase in the solvent extraction

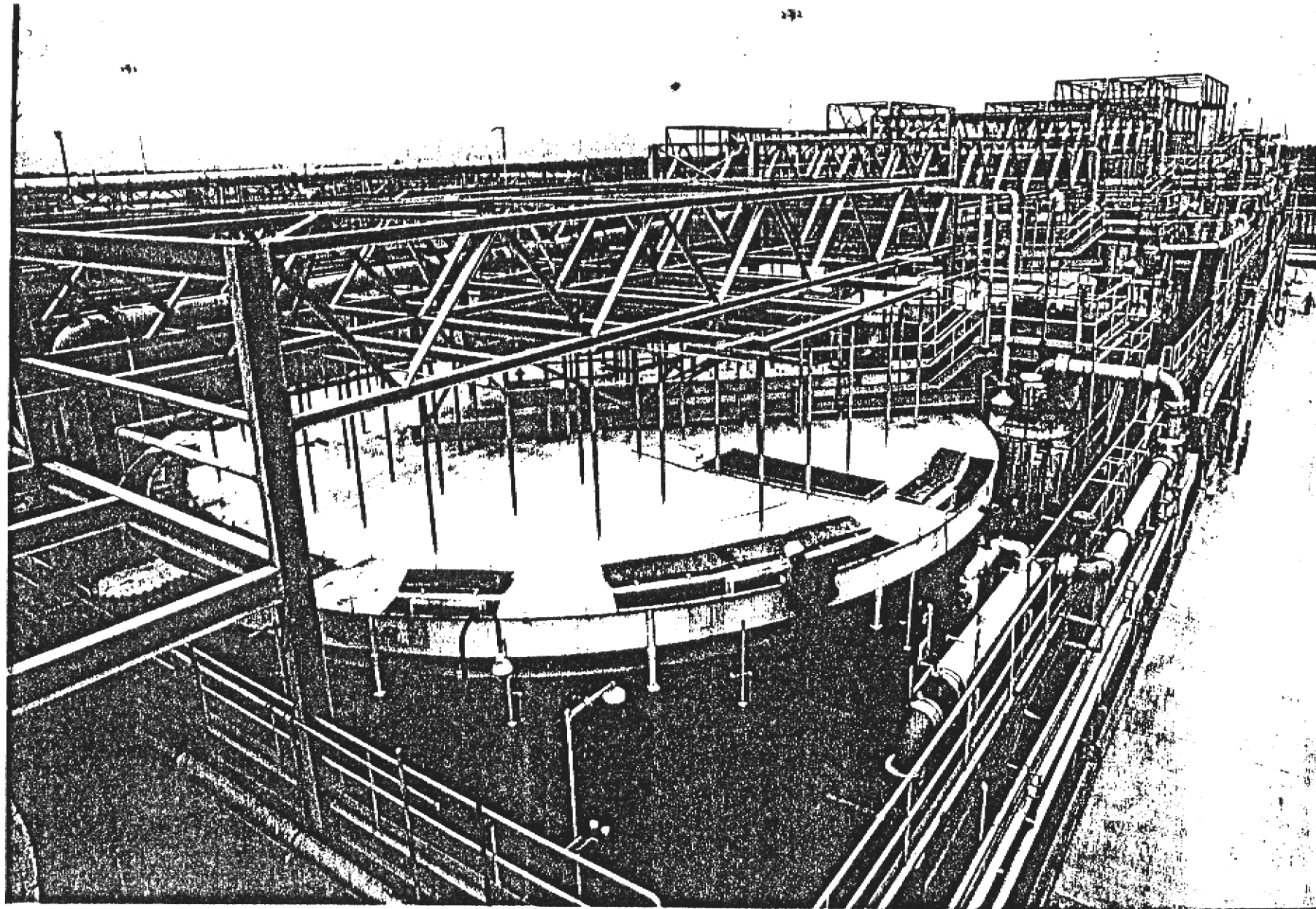


FIGURE 10

INTERFACIAL CRUD RATE AS FUNCTION OF ACID COLOR

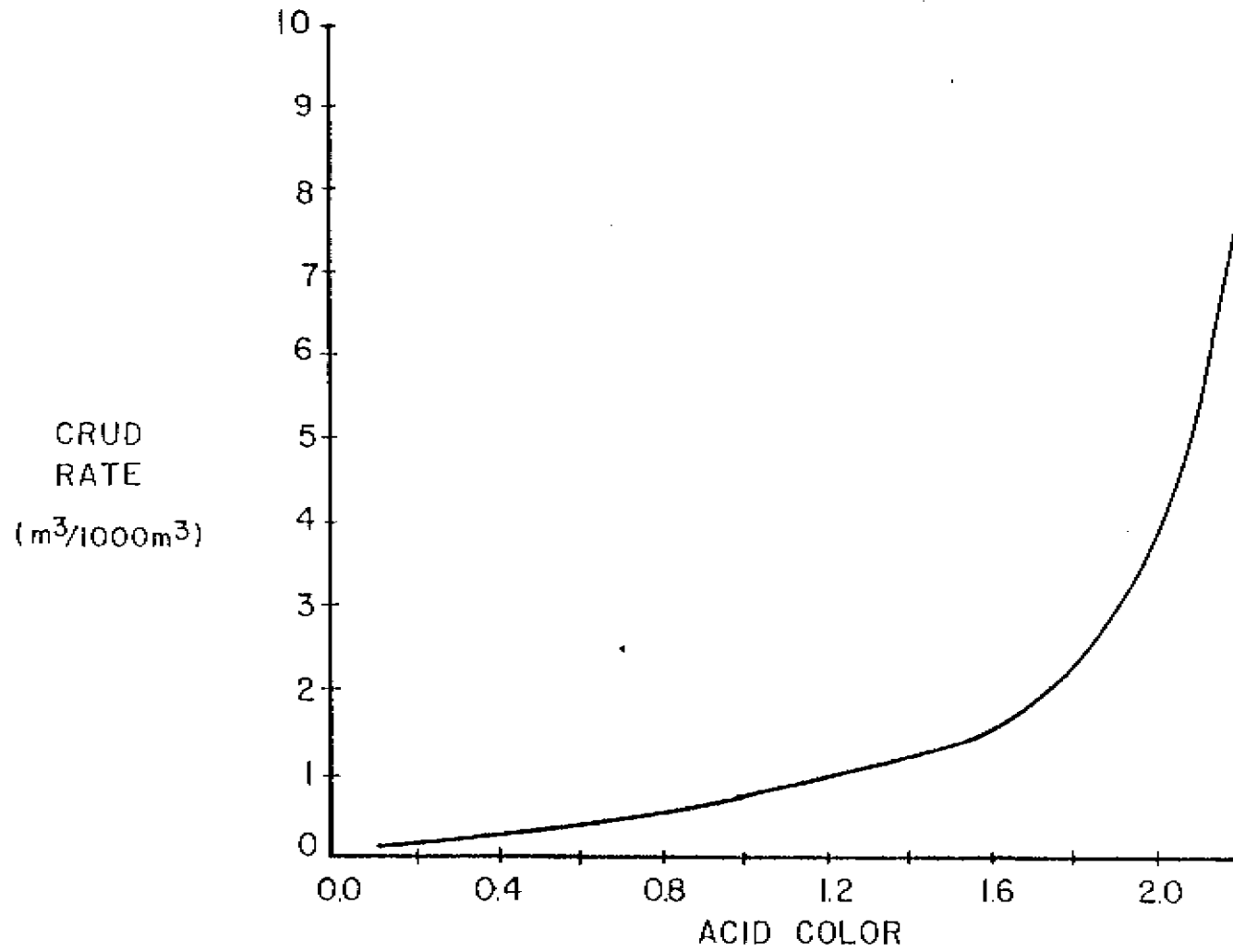


FIGURE II

circuit to form excessive crud, which must be removed in some fashion eventually. At New Wales minimal crud treating facilities are required due to the low potential for crud formation. The small amount formed is continuously removed.

Acid Post-Treatment

It is extremely important that organic entrainment be minimized in the phosphoric acid (raffinate) returned to the existing plant. Since most of the down stream equipment is rubberlined, excessive organic could result in substantial rubber damage, it is equally important to minimize solvent losses because of the high cost of the solvents.

At New Wales, several steps are taken to insure that entrainment is minimized. As indicated earlier, the last mixer-settler unit operated organic continuous in order to reduce the degree of entrainment at this point. The effect of organic versus aqueous continuous operation on organic entrainment is shown in Table I.

TABLE I
EFFECT OF AQUEOUS VS. ORGANIC CONTINUOUS OPERATION
ON ORGANIC ENTRAINMENT IN ACID

<u>LOCATION</u>	<u>ORGANIC ENTRAINMENT IN ACID (ppm v)</u>	
	<u>AQUEOUS CONTINUOUS</u>	<u>ORGANIC CONTINUOUS</u>
LAST MIXER SETTLER	1600	300
RAFFINATE SETTLER DISCHARGE	530	130

Acid from the last mixer-settler unit enters the raffinate settler, which is essentially a large de-entrainment vessel to remove the bulk of the organic material. From the raffinate settler, the acid enters modified flotation cells for final entrainment removal.

The maximum allowable organic entrainment level is 50 parts per million by volume. After post-treatment, the raffinate containing less than 50 ppm of entrainment, is returned to the P₂O₅ facility.

The loaded strip acid from the primary circuit is transferred to the secondary circuit. The basic steps in this system are shown in Figure 12. The design uranium concentrations of the major streams are indicated also.

Secondary Extraction and Strip

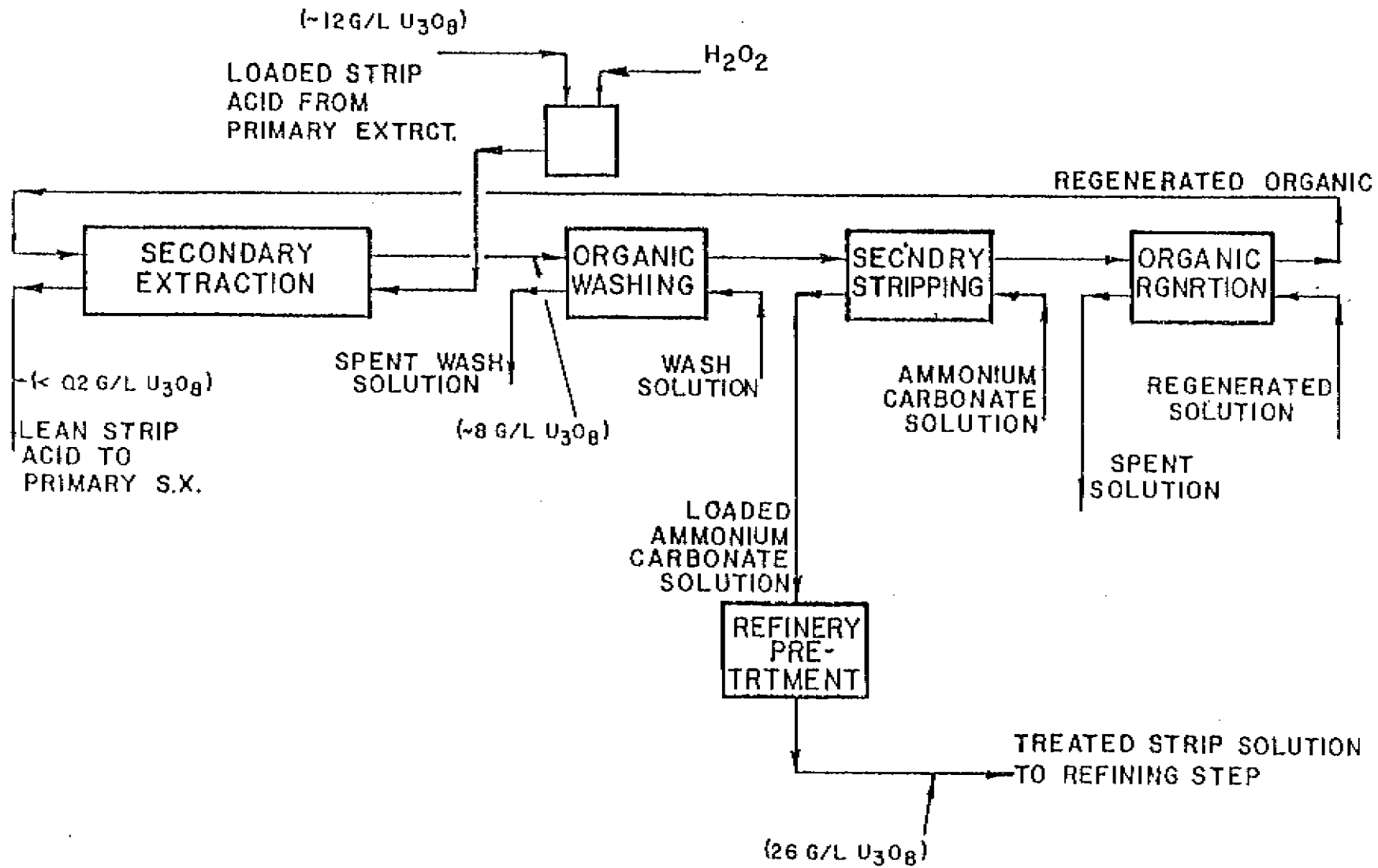
Loaded strip is first oxidized with H₂O₂ then sent through a second DEHPA-TOPO extraction circuit. Rectangular mixer-settlers are used to transfer uranium from the acid to the organic phase.

Lean (spent) strip acid is returned to the primary extraction circuit. Pregnant (loaded) organic is sent through a water wash to remove any entrained P₂O₅ before transfer to a secondary stripping circuit. The water washing step is employed primarily to remove any entrained and/or dissolved phosphoric acid from the pregnant secondary organic. This insures that P₂O₅ contamination in the final product is kept below normal specification limits.

In the secondary strip circuit, the pregnant organic is mixed with a dilute ammonium carbonate solution to remove the uranium from the organic, while the DEHPA is converted to an ammonium salt. A weak ammonium carbonate solution is used in order to avoid uranium precipitation in this circuit.

IMC/PRAYON URANIUM RECOVERY PROCESS

SECONDARY EXTRACTION/STRIP SYSTEM



7 - 21

FIGURE 12

Barren organic is regenerated and returned to the secondary extraction circuit. Regeneration is accomplished using a mineral acid which supplies H^+ ions to the DEHPA, thus reconverting it to the acid form.

Loaded alkaline strip solution is next treated in a proprietary processing step in order to reduce the pH, remove CO_2 and prepare the solution for uranium precipitation. This step is extremely critical to the operation.

Uranium Precipitation and Drying

At New Wales, a modification of the United States Bureau of Mines Peroxide Precipitation Technique is utilized. The use of hydrogen peroxide has been discussed in various publications and is in use in some conventional uranium operations. (15, 16, 17) Figure 13 shows the primary steps involved in this system which is called the Refining Operation.

A continuous precipitation circuit is utilized in this proprietary system. Hydrogen peroxide is added to the prepared strip solution, the pH is adjusted and uranyl peroxide is precipitated.

The uranium slurry is clarified, washed, centrifuged, then dried. This technique results in a uranyl peroxide product of exceptional purity, since the peroxide route is quite selective for uranium under the conditions employed. As a general rule, the concentration of various contaminants in the final product is significantly below allowable limits established by the UF converters. Table II shows typical analysis of yellowcake produced via this technique.

TABLE II
YELLOWCAKE ANALYSIS

<u>COMPONENT</u>	<u>% BY WEIGHT IN DRY YELLOWCAKE</u>
U	68.2
V	<0.01
P	0.009
F	0.02
Mo	<0.01
S	0.08
Fe	0.001
Si	<0.01
Mg	NONE DETECTABLE

Recovery of yellowcake hovers around 98% of the uranium extracted in the secondary stripping circuit. This high recovery indicates that the IMC/Prayon system is indeed a special technology.

The joint IMC/Prayon technology, however, allows the use of other precipitation methods, depending on Client requirements. The Prayon plant (located in Belgium) uses a slightly different technique, in which a uranyl hydrate compound is precipitated. Again, a high purity product is produced.

With respect to radioactivity, most of the hazardous radionuclides, radium and its daughters, are removed from the process in the acid plant with the gypsum. The only problem in the uranium recovery plant is from dusting in the drying and packaging operations. Sophisticated methods to prevent the inhalation of dust by the workers and dust collectors to prevent its spread to outlying areas have been installed. Health monitoring procedures have been set up more stringent than the conditions and limitations specified by the State of Florida.

IMC/PRAYON URANIUM RECOVERY PROCESS URANIUM PRECIPITATION AND DRYING

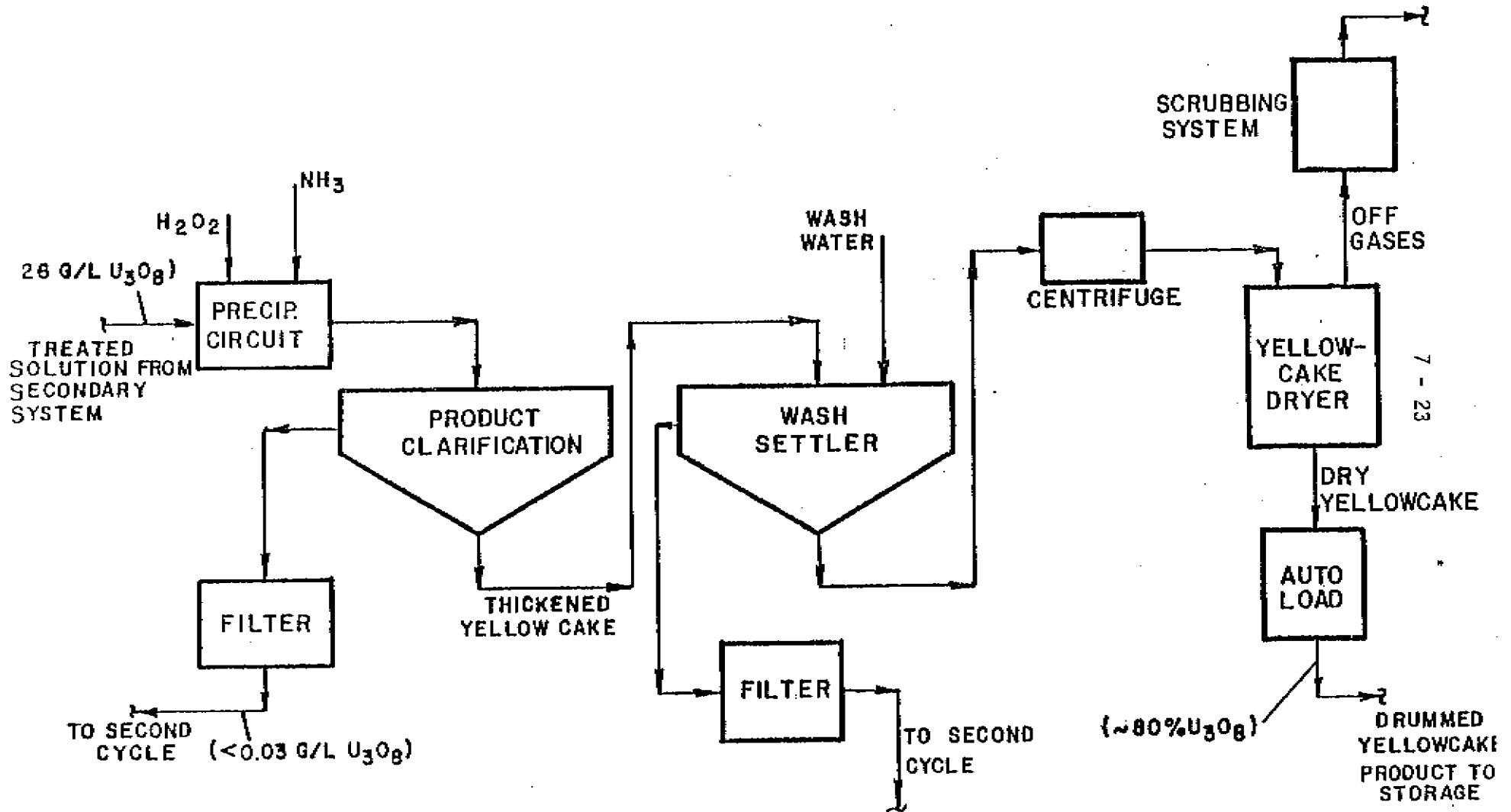


FIGURE 13

TECHNOLOGICAL VARIANTS EXPERIENCED IN THE PRAYON PLANT

Although the basic flow sheet remains identical, the technological application may vary according to local conditions such as :

- Type of rock or rocks, their possible analytical variation in the course of time.
- Water circuit arrangement and water quality (acidity, temperature).
- Possibility of sludges recycling.
- Plant capacity.
- Construction materials availability.
- Local regulations for industrial safety and health as well as for environmental protection.

We have experienced many such technological variations in the Prayon plant, built in Belgium and comprising :

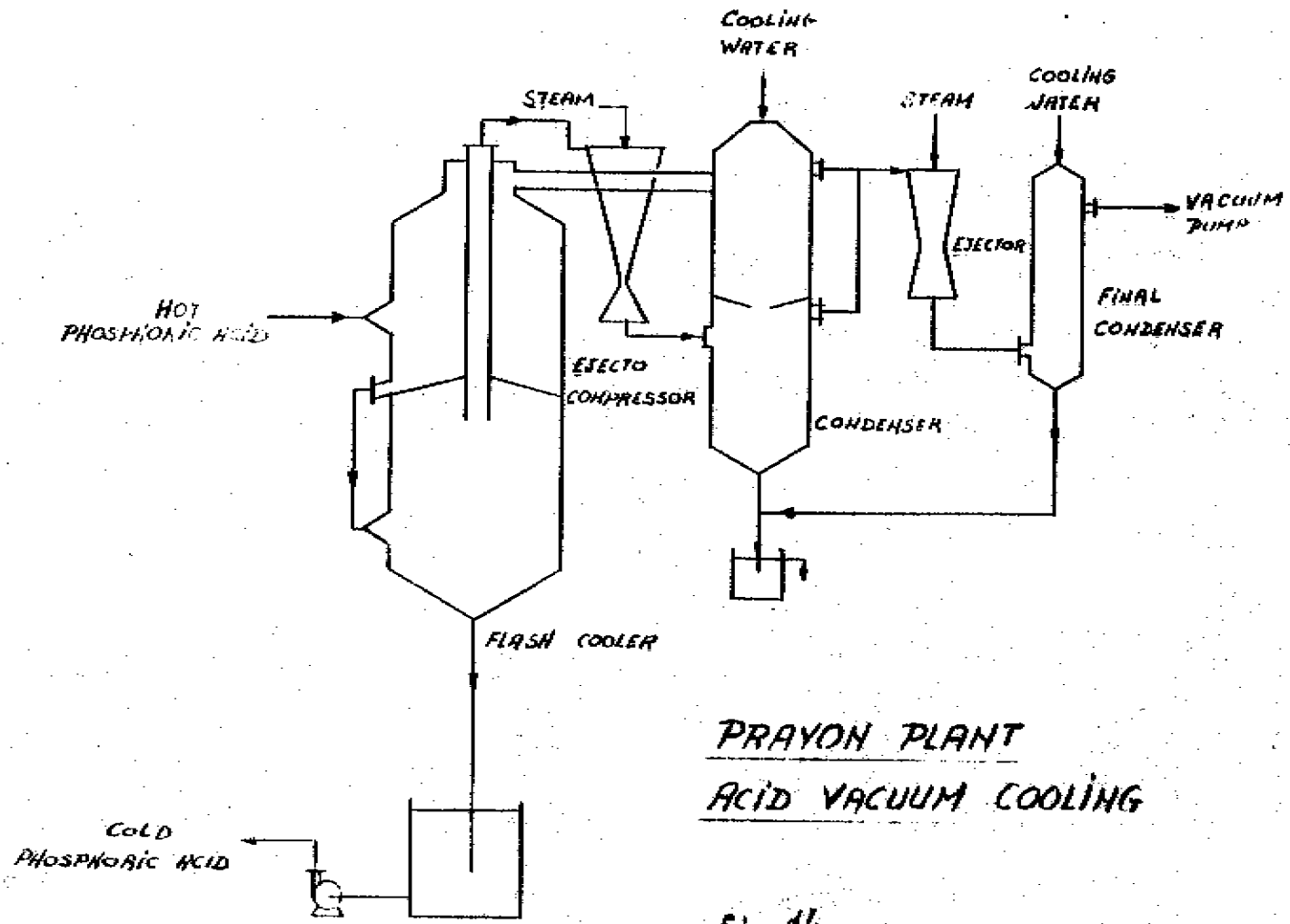
- The acid clean-up and the first cycle in the Puurs plant.
- The second cycle and the precipitation-separation of the yellow cake, in the Engis plant, 125 km from Puurs.

Some choices were made, which are different from IMC's in New Wales and which are described hereafter :

- Acid clean-up :
 - . The filter acid has a higher P₂O₅ content (30 to 32 % P₂O₅ versus 27 to 29 %) due to, among other reasons, the recycling of concentrated sludges. It was found justified to compensate the resulting drop in extraction coefficient by lowering the temperature of the acid fed to extraction : 35°C instead of 49°C in New Wales. For the same reason, the temperature of the stripping section was increased to 55°C versus 49°C in New Wales. Moreover the desaturation of the acid has been especially well achieved to limit the crud formation and the scaling in the mixer-settlers; this has been achieved by cooling the acid first to 25°C, aging it and reheating to 35°C after solids separation and before contacting the solvent.
 - . Industrial water temperature is too high in summertime to allow the cooling of acid down to 25°C and there is no pond water available for heat exchanger descaling. For these two reasons, vacuum cooling was preferred. (Figure 14).
 - . In the Puurs plant, due to the high quality of acid produced, sludges recycling is high and it was decided not to increase it any more with the additional clean-up of the acid, but to take this opportunity to decrease it. That is why the solids separation is not done by settling, as in New Wales, but by vacuum filtration.
- Cycle I :
 - . Due to the plant capacity, rectangular mixer-settlers with pump mixers are used.
 - . The DEHPA-TOPO concentration is 0.5 molar DEHPA and 0.075 molar TOPO versus 0.5 molar DEHPA and 0.125 molar TOPO in New Wales in order to reduce the consumption of the expensive TOPO solvent while keeping a good extraction coefficient.

- . In the stripping section, an interstage reduction system is used in addition to the primary reduction of the strip acid in order to control re-oxidation during stripping and to limit the iron content of the strip acid.
This interstage reduction is achieved by intermittently immersing baskets containing iron scraps in the syphon compartment of the mixers-settlers.
- . All vessels and equipment in the first cycle, as well as in the second cycle are made of stainless steel.
- Acid post treatment :
Organic removal from the acid is accomplished by a lamella type settler followed by active carbon columns. Other alternatives like flotation and centrifugation are under investigation in order to determine the profitability of solvent recovery.
- Secondary cycle :
 - . The flow sheet is essentially the same as New Wales except that the stripping operating conditions are such that iron is made to precipitate in the stripping settlers and is removed by a close filtration circuit.
 - . DEHPA-TOPO concentration is 0.3 molar DEHPA and 0.075 TOPO in order to accommodate the stripping operating conditions.
- Uranium precipitation
Uranium precipitation out of the strip alkaline solution is accomplished by decreasing the pH. This is achieved by destroying the carbonate in a batch evaporation. The final product corresponding to the formula $3\text{UO}_3 \cdot \text{NH}_4 \cdot 5\text{H}_2\text{O}$ is filtered on a press filter and drummed before shipment to the conversion plant.
Purity of the product is extremely high and in fact very close to the "nuclear grade" specification of the converters.
If requested, the filter cake may be dried or calcined; however, ending with a wet cake eliminates the risk of dust inhalation by the workers and greatly reduces the environmental protection requirements.

IMC / PRAYON URANIUM RECOVERY PROCESS.



PRAYON PLANT
ACID VACUUM COOLING

Fig 14

IMPACT OF URANIUM RECOVERY OF PHOSPHORIC ACID COMPLEX AND FUTURE POTENTIAL

Obviously, the extensive acid clean-up employed in this process will result not only in a smoother solvent extraction operation, but also in certain down stream impacts and significant future potential. A brief discussion of these factors follows:

The phosphoric acid (raffinate) leaving the uranium extraction facility is extremely clear, low in solids and green. The amount of solids precipitated in down stream processing circuits, such as phosphoric acid evaporation, will decrease as a result of the acid clean-up system. In addition, indications are that green phosphoric acid results in less scaling in 30% phosphoric acid systems than brown acid. It appears that the thickness of pipe scale in green acid service is less than 20% of that associated with brown acid.

During evaporation, the amount of solids precipitated should decrease to some extent, as a result of the acid cooling and clarification steps in the uranium circuit.

Figure 15 shows the level of solids in the evaporator circuit before and after uranium recovery. It should be pointed out that New Wales uses three stages of evaporation and clarifies the acid at the 40% level. It can be seen that the amount of solids in the 54% acid has decreased as a result of the clean-up system.

Future Potential

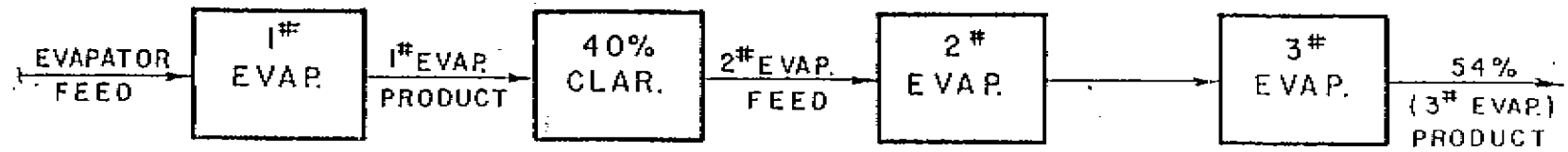
With the advent of green Florida phosphoric acid, there is a potential for exploring new processing areas. A green phosphoric acid should provide an ideal feed for other solvent extraction processes since it minimizes the amount of additional pretreatment required. Examples are technical grade phosphoric acid and magnesium removal by solvent extraction.

The extraction of uranium from phosphoric acid is a burgeoning industry that will have a major impact on the Phosphate Chemicals Producers in the future. The IMC/Prayon technology offers a proven economic route to pre-treat wet process phosphoric acid for solvent extraction and to recover efficiently the uranium as a high grade uranium oxide, quite suitable for converting to a usable needed source of energy.

Acknowledgement

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P₂O₅ EVAPORATION CIRCUIT-SOLIDS PROFILE
FOR BROWN AND PRETREATED GREEN ACID



7 - 28

% SOLIDS BY WEIGHT IN ACID STREAM (1 WEEK AVERAGE - WEST EVAPORATOR TRAIN)

	EVAP. FEED	1# EVAP. PRODUCT	2# EVAP. FEED	54% (3# EVAP. PRODUCT
REGULAR BROWN ACID WEEK OF 8/26/79	1.08	2.29	1.52	4.11
PRETREATED GREEN ACID WEEK OF 10/7/79)	0.49	1.61	1.32	2.26

FIGURE 15

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TA/80/7 The IMC/Prayon uranium recovery process by F.T. Nielsson, IMC, United States, A. Dubreucq, Société de Prayon, Belgium

DISCUSSION : (Rapporteur D.W. Leyshon, Jacobs Engineering Inc., United States)

Q - Mr. I. KOTLAREVSKI, Gardinier S.A., France

- a) To our knowledge, the increase in the iron content resulting from phosphoric acid reduction represents about 10% of the iron initially contained in the rock. Does your process introduce other impurities which would explain your granulation problems? since we have none.
- b) The President of IMC announced that New Wales investments in uranium recovery amounted to \$ 184 million. Can you give the detail of the investment as well as the capacity of each section of the unit?

- A -
- a) Nowhere was it said that IMC had granulation problems. On the contrary, the phosphoric acid quality is improved after uranium extraction which has a beneficial effect on all the subsequent manufacturing stages.
 - b) The authors do not know accurately the total value of the investment nor its distribution.

This investment includes the following plants:

CF at Plant City: "Acid clean-up" and "first cycle" sections: 680,000 t/yr P_2O_5 .

CF at Bartow: "Acid clean-up" and "first cycle" sections: 720,000 t/yr P_2O_5 .

IMC at New Wales: "Acid clean-up" and "first cycle" sections: 1 million t/yr P_2O_5 .

"Second cycle" and "refinery" sections: 2,160,000 Lb U_3O_8 /yr.

Q - Mr. O.H. LIE, Norsk Hydro, Norway

- a) In the decoloring process, how do you regenerate the activated carbon?
- b) What is the activated carbon make-up (\$/t P_2O_5)?

- A -
- a) Humates are regenerated using the same procedure used for phenols.
 - b) Carbon make-up was estimated to be \$280/t P_2O_5 but is running much less in practice.

Q - Mr. A. VILLARD, APC, France

How do you regenerate activated carbon?

- A - Activated carbon is regenerated chemically and not thermally.

Q - Mr. B. AVENBERG, Supra, Sweden

- a) Page 7-16. How do you control or measure the Fe^{2+} level in the oxidation stage and how is the amount of hydrogen peroxide addition controlled?
- b) Page 7-17. The Fe^{2+} concentration in the reduced acid: How is that measured?
- c) Page 7-25. Can you give more information about the use of lamella type settler, the way it's used and separation efficiencies?

A - By Fe titration using sodium dichromate.

IMC does not use lamellas.

Q - Mr. I. EZAHR, OCP, Morocco

- a) Did you find an optimum iron quantity to be used? Is it the same for each extraction stage? Is this amount not a nuisance in the second extraction stage during oxidation? (Reference to the formation of Fe^{3+} salts).
- b) Is the knowledge of the Fe^{2+} content sufficient to control the extraction of U^{IV} ?
- c) In view of the quick conversion of Fe^{2+} into Fe^{3+} (even in the air), do you use a quick analytical method for Fe^{2+} ?
- d) What is the phase ratio in the second extraction with a diluted acid?

A - a) It is true that an excessive addition of iron in the second extraction leads to the formation of insoluble ferric salts in the mixer-settlers of the second extraction and in the equipment following the oxidation in the second stage. The importance of the problem was largely reduced by the incorporation of a system called "Interstage reduction" which consists in adding only a minimum amount of iron directly in the mixer-settlers. This amount is adjusted to take account of the amount of uranium to be reduced and to make up for the natural reoxidation of the existing iron.

This enables us to reduce strongly the impact of this phenomenon and we believe this problem will be completely solved at the end of this year.

- b) This knowledge is sufficient, but we prefer to use the measure of the potential since this method is more accurate and quicker.
- c) We use the colorimetric method.
- d) A/O ratio r 2/1.

Q - M. M. BERGERET, Gardinier, France

- a) Why did you obtain only 50-75% uranium recovery from phosphoric acid using pyrophosphate esters while our industrial operation in Tampa shows rates varying from 90 to 95%?

- b) Among the reasons for selecting the TOPO-D₂-EHPA process, what is the factor which compensated the need for an organic purification of fresh phosphoric acid since, in the OPAP type processes, this is not necessary?
- c) What is the reference of your U₃O₈ price curve on page 3 of your paper?

- A -
- a) The authors are not personally aware of this operational period which dates back + 25 years. However, the low extraction recovery at that time was attributed to operational difficulties resulting from the fact that the equipment used was not adapted and from the quick degradation of the solvent.
- b) The presence of organic matter in phosphoric acid leads to the formation of cruds during the extraction whatever the process used. These cruds are a nuisance for the phase exchange and separation operations and their removal, which, in practice, is not easy, results in solvent losses. The acid refining according to the IMC-Prayon process allows to eliminate or, at least, to minimize the problem.
- c) The curve represents the variation of the exchange value for U₃O₈ defined in the monthly publication "Nuclear Exchange Corporation".

Q - Mr. T.J. PEARCE, Estech Chem. Corp., United States

Does Prayon use carbon granules in their process and, if so, what do you do with the spent carbon?

- A -
- Yes, Prayon uses activated carbon in their process. In view of the type of acid processed, the regeneration frequency of this carbon is very low and, hence, its life is very long. As a result, the problem of disposing of spent carbon will not arise before a few years. In view of the small amounts concerned, a thermal regeneration is probably not economically justified and other possibilities are presently under investigation.

Q - Mr. M. SMILJANA, INA, Yugoslavia

- a) What correlation do you find between acid colour, amount of formed emulsion and total organic carbon (or equivalence)?
- b) What does it mean - in your paper: "refinery pre-treatment of loaded ammonium carbonate solution after secondary extraction/stripping circuit?"

- A -
- a) We did not have the capability to analyze for total organic carbon when this report was written.
- b) This is proprietary.

Q - Mr. J.D. CRERAR, Fisons Ltd, United Kingdom

What differences in extraction rates have been experienced, between:

- a) Florida rocks of differing P₂O₅ concentrations: (mentioned on p. 24)? Does export of beneficiated grade distort economies in Europe compared with USA?

b) Florida and similar grade of Morocco rock?

A - Acid concentration affects extraction of uranium, not phosphate content of rock.

Higher BPL rocks usually have a lower U_3O_8/P_2O_5 content.

Q - Mr. N. ROBINSON, Fisons Ltd, United Kingdom

Do the residual solvent impurities in the phosphoric acid affect gypsum filtrability? If there are no effects with Florida rock, what is the position with other rocks?

A - No difference has been noted after one year's operation.

Q - Mr. R. VAN HARDEVELD, D.S.M., Netherlands

a) On page 4 of your paper, you state that the uranium concentration in the process liquor is increased by a factor of 60. Therefore, the strip acid is only one-sixtieth of the primary acid. This means that only 1.5% i.e. (1/60) of the iron must be added.

Can you explain this statement any further, since in my opinion the amount of uranium to be reduced from 6+ to 4+ remains the same and hence the amount of iron to be added?

b) On page 5, you indicate that returning green acid to the phosphoric acid facility results in certain processing benefits. Can you indicate which?

c) Can you comment on why you prefer to use the expensive mixer-settler system for the extraction forward and backward, and not such a simple apparatus as a single pulsed packed column for each of these steps. The height of the pulsed packed columns can be adjusted to the desired number of transfer units, whereas the scaling up factor is simply one.

A - a) The amount of U in the acid is very small compared to the amount of iron. With the acids we have tested it is the Fe^2 to Fe^3 ratio that is important, not the amount of Fe.

b) These are spelled out in the paper, like less scaling in pipes.

c) No one in our experience uses columns for 5000 liter/min. rates.

Q - Mr. J. FROCHEN, COFAZ, France

a) Could you tell us what the crud looks like and how you dispose of it in the settlers, continuously or batch wise?

b) Concerning the purification of the acid by activated carbon, you say that in a cleaning cycle, the colour varies from 0.1 to 0.6. Is it not troublesome in some way, and did you consider using a more continuous way, as it exists in the demineralisation of boiler feed water. How many columns do you use, and how do you regenerate the spent carbon?

A - a) Crud can float, settle or be interfaced in a settler. It appears to be

- A - made up of humates, an iron-potassium-phosphate compound and organic. We are trying various means for treating it before disposal.
- b) We use a continuous system. In the pilot plant, four columns were on line, with a fifth being regenerated. In the big plant, 2 columns are on line with a third being regenerated. Regeneration is done chemically.