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URANIUM RECOVERY IN A HEMI-DIHYDRATE PROCESS OF CONCENTRATED ACID PRODUCTION

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Since the outset of uranium recovery, a considerable attention has been given to phosphate rock as uranium resources. In the 1940's, extensive researches were carried out on uranium recovery from phosphate rock - phosphoric acid and then solvent extraction of uranium from phosphoric acid was considered most promising. In the 1950's, the extraction process using OPPA (octyl phenyl piro phosphoric acid) was established and commercialized in the United States. In the 1960's, however, the recovery of uranium from phosphoric acid lost its attractiveness generally due to the decline in the price of uranium.

However, Oak Ridge National Laboratories (ORNL, U.S.A.) researched into the uranium extraction technology from phosphoric acid fundamentally over again and in the early 1970's they succeeded in developing two new extraction processes (D2EHPA-TOPO system and OPAP system).

Just at that time, energy costs went up rapidly and this brought about a spurt of interest in the recovery of uranium from phosphoric acid. Then, the uranium recovery based on the ORNL technology has been studied widely in many countries of the world. Several companies have already carried out commercialization of the process and reportedly several others are planning to commercialize it.

Meanwhile, one of the important themes in the phosphoric acid industry during the 1960's was development of a process capable of directly producing high concentrated phosphoric acid of more than 40 % P2O5. Following TVA's foam process and clinker process, hemihydrate process and hemi-dihydrate process were developed to meet such requirement by several companies and these processes were brought into commercial operation successively from the late 1960's to the early 1970's.

"Recovery of uranium from phosphoric acid" and "direct production of high concentrated phosphoric acid" are both the technical developments closely related to energy problem, and as these are independent with each other, combining of the two would offer more advantages.

However, empirically, the combining of the two technologies indicated a basic difficulty. That is, as shown in figure-1, the distribution coefficient of uranium in solvent extraction depends on the concentration of phosphoric acid and it substantially lowers when the phosphoric acid concentration becomes higher than 30% P2O5. Therefore, in order to recover

uranium from high concentrated phosphoric acid, it is neces-
sary either to employ more extraction steps or to seek more
powerful extractant. Further, in extraction of uranium from
high concentrated phosphoric acid, it is said that efficiency
of aqueous and organic phase separation, which is another
important factor, is decreased. For these reasons, combina-
tion of high concentrated P2O5 process and uranium recovery
has not yet been established industrially. But, TVA and
Earth Science Inc. carried out development works for such
technology and reported the successful results.

We, as a phosphoric acid producer, have studied recovery
of uranium from high concentrated P2O5 process and obtained
fair prospects that it would be not only feasible but also
more economical than extraction from lower concentrated phos-
phoric acid in conventional dihydrate process. Here we report
the results of our study.

To facilitate better understanding of our research re-
sults, we would like to first introduce the high concentrated
P2O5 process we evaluated. Figure-2 is a schematic flow dia-
gram of hemi-dihydrate process as practiced by Nissan. The
process occurs in two stages, a hemihydrate stage, which con-
sists of hemihydrate reaction and filtration section, followed
by a dihydrate stage, which consists of hydration and filtra-
tion section. In the hemihydrate stage, phosphate rock is
treated with a mixture of phosphoric acid and sulfuric acid
to produce phosphoric acid and calcium sulfate hemihydrate.
The product is recovered from hemihydrate filtration section
and its concentration is 40 to 50 % P2O5. In the dihydrate
stage, the hemihydrate is further processed by redissolving
and hydration thus forming calcium sulfate dihydrate, namely
gypsum. The liquid/solid separation on the dihydrate filter
yields the by-product gypsum and filtrates that are recycled
back to the front end of the process. The unreacted P2O5 con-
tained in gypsum is less than 2 % of raw material P2O5. This
process comprises of two parts of different reaction condi-
tions, namely hemihydrate stage and dihydrate stage; each has
different acid concentrations and accordingly chemical condi-
tions are also different. These two stages are combined by
cake washing in hemihydrate filtration section, thereby
material balance is maintained. In addition, the substance
which is entrained in hemihydrate and is released in hydration
section, for example P2O5, is returned to hemihydrate reaction
section as washing acid.

Then we would like to proceed to report the results of
our study as follows:

(1) Measurement of uranium concentration in each section of
a commercial plant.

(2) Uranium balance in the process at the time of recovering
uranium from phosphoric acid.

Figure-3 indicates the uranium concentration in each
section of the commercial plant. The compositions of feed
phosphate rock, product and calcium sulfate are given in
Table-1. Figure-3 shows:

(1)   In hemihydrate reaction section, uranium is mostly distributed on solid side.

(2)   In hydration section, uranium is mostly distributed on liquid side.

(3)   However, when the uranium concentration in liquid in hydration section becomes higher, the amount of uranium which returns to hemihydrate reaction section as dissolved in washing acid is increased and eventually the greater part of input uranium is discharged into the product overall.

In view of these facts the above-mentioned fact that as shown in Figure-1, uranium extraction is very easy in the case of low phosphoric acid concentration because the lower the concentration of phospohric acid is, the more uranium will move into extraction solvent, we conceived the idea of uranium recovery from the filtrate in hydration section of high concentrated P2O5 process.

As the technology for extraction of uranium from dilute phosphoric acid has already been established, we utilized it to study the following in a bench scale unit:

(1)   Will extraction operation exert any adverse effect upon phosphoric acid manufacturing process?

(2)   In case uranium is extracted from liquid in hydration section, how far will uranium into solid in hemihydrate reaction section be decreased? Otherwise, how much uranium can be recovered?

As shown in Figure-5, test flow was designed with addition of uranium extraction section to Figure-2. As uranium extraction process, ORNL's D2EHPA-TOPO-kerosine system solvent process was employed. The test was conducted by continuous operation for hemihydrate reaction section and batchwise for others. The feed phosphate rock used was an equivalent to the rock specified in Table-1.

Figure-4 shows the uranium concentration balance after 60 hrs. of operation with no extraction of uranium.

Figure-5 shows the uranium concentration balance after 150 hrs. of operation (90 hrs. from the commencement of uranium extraction).

As it is apparent from Figure-3, 4 and 5, there is a fixed relationship between uranium concentration in liquid and uranium concentration in solid; i.e. when the uranium concentration in liquid is decreased, that in solid is also decreased. Supplementary the data at the operation time of 90 hrs. and 120 hrs., the relationship between the uranium concentrations in liquid and solid in hemihydrate reaction section is as plotted in Figure-6 where the horizontal axis shows uranium concentration in liquid and the vertical axis shows uranium concentration in solid. A is the data obtained in the commercial plant and 1, 2, 3 and 4 are the data of laboratory test. To determine a regression formula from this, where the uranium concentration in liquid is X ppm, the uranium concentration in hemihydrate is $0.34X + 54$ ppm.

Assuming the uranium concentration in raffinate to be 2 ppm, the uranium concentration in liquid in the reaction stage is 17.2 ppm and that in hemihydrate is 59.8 ppm as calculated from process mass balance, and this point is shown in Figure-6.

The unrecovered uranium is 20 % in total of uranium in product and that in gypsum, 13 % and 7 % of uranium content in phosphate rock respectively. Then, the uranium recovery efficiency is expected to be 80 %, if handling loss is not taken into account.

In addition, it is noted that no adverse effects were caused by combining uranium extraction process with high concentrated P2O5 process within the scope of this test.

In the foregoing, we reported that it is possible to attain 80 % uranium recovery by combining the existing uranium extraction process with hemi-dihdyrate route high concentrated P2O5 process.

When it is assumed that the acid from phosphoric acid plant with a capacity of 1,000 t-P2O5/d using Florida 72 BPL rock is applied to uranium recovery process, the acid source and the properties of the acid for extraction of uranium are listed in Table-2.

In comparison to the conventional uranium recovery from 30 % P2O5 acid in conventional dihydrate process, the uranium recovery process from the dilute phosphoric acid such as 15 % P2O5 acid in hydration section of hemi-dihydrate route high concentrated P2O5 process such as Nissan C process will have the following advantages.

(1)   The acid for extraction of uranium is primarily pretreated or clarified and suspending material is removed from the acid to produce a clean phosphoric acid using a gravitational sedimentation method in general. Sedimentation velocity of suspending material is proportional to the difference in specific gravity between solid and liquid and is inversely proportional to viscosity of liquid in accordance with Stokes' equation concerning such gravitational sedimentation.

In addition, the size of plant equipment in this step is also proportional to the volume of material flowing through the recovery plant. As suspending material contains mainly gypsum, the size of plant equipment in this step of 15 % P2O5 acid uranium recovery process will become much smaller than that in case of the use of 30 % P2O5 acid.

(2)   When organic material is removed from the acid to produce a clear phosphoric acid material by passing through activated carbon columns, necessary quantity of activated carbon will be reduced in 15 % P2O5 acid uranium recovery process, otherwise the length of life for regeneration of activated carbon will be increased.

(3)   The distribution coefficient is related to the concentration of phosphoric acid and extraction solvent. The distribution coefficient of 30 % P2O5 acid and 15 % P2O5 acid is 1.5 and 40 respectively as shown in Figure-1.

If 90 % of extraction coefficient of uranium in the acid is achieved maintaining the volumetric ratio of the acid to extraction solvent at 2:1, uranium extraction from 15 % P2O5 acid will require fewer stages than with the plants commonly recovery uranium from 30 % P2O5 acid.

Consequently the size of plant equipment and the volume of extraction solvent will become much smaller.

In addition, the loss of extraction solvent will be significantly minimized, as it is possible that concentration of extraction solvent is reduced.

(4) Efficiency of acid and organic phase separation is incorporated into the design of the plant equipment. Such efficiency in 15 % P2O5 acid uranium recovery process will be significantly improved compared to that in case of the use of 30 % P2O5 acid.

(5) Corrosion rates of stainless steel in 15 % P2O5 acid of the hydration section of high concentrated P2O5 process are far less than those in case of the use of 30 % P2O5 acid. Accordingly the use of 15 % P2O5 acid is of great advantage to the quality of materials.

(6) The deterioration of extraction solvent in 15 % P2O5 acid uranium recovery process is less compared to that in case of the use of 30 % P2O5 acid. Consequently unit consumption of extraction solvent will be decreased.

In conclusion, let us reiterate that: "Recovery of uranium from phosphoric acid" and "direct production of high concentrated phosphoric acid" are both the technical developments closely related to energy problem and combining of the two would offer more advantages. The present work should be regarded as an encouragement to the uranium recovery by combining the existing uranium extraction process with hemidihydrate route high concentrated P2O5 process such as Nissan C process.

Table-1 Chemical Analyses of Phosphate Rock, Product Acid, Hemihydrate and Byproduct Gypsum

	Phosphate Rock	Product Acid	Hemihydrate Cake	Byproduct Gypsum
$T-P_2O_5$	32.21	46.50	2.37	0.34
$W-P_2O_5$	-	-	1.17	0.16
CaO	48.31	-	36.13	31.42
SO_3	1.33	3.80	49.03	44.90
CO_2	4.14	-	-	-
F	3.99	0.56	1.3	0.98
SiO_2	5.32	0.16	2.96	2.57
Fe_2O_3	0.95	1.21	0.04	0.07
Al_2O_3	0.85	0.92	0.33	0.13
MgO	0.40	0.55	0.03	0.01
Na_2O	0.60	0.11	0.56	0.38
K_2O	0.28	0.03	0.25	0.17
Cl	0.004	0.004	-	-
$C-H_2O$	-	-	7.18	19.95

Table-2 <u>Properties of the Acid for Uranium Recovery Process</u>

Process	Acid Source	P2O5 Concen- tration %	Specific gravity	Viscosity C.P.	Volume of Acid t/d
Nissan C	Hydration Acid (Filtrate acid from dihydrate filtration)	15	1.16	1.2	3,235
Conventional Dihydrate	Product Acid	30	1.35	3.2	3,333

Figure-1 Effect of H_3PO_4 Concentration on Uranium Extraction

Uranium
extraction
coefficients
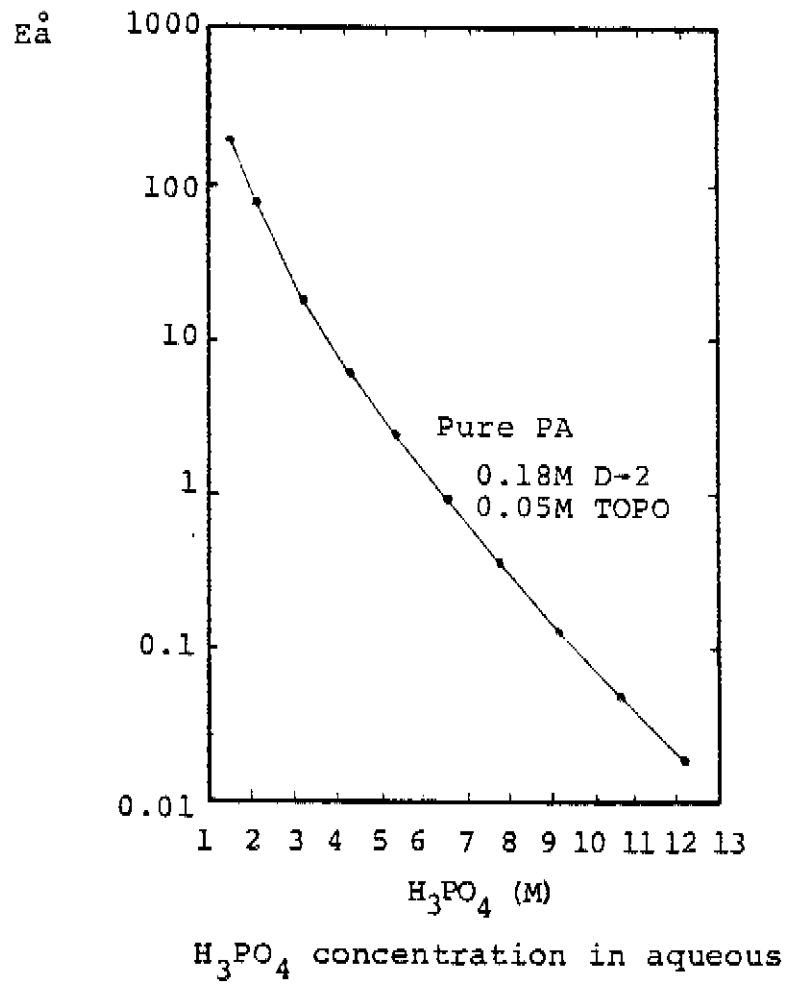

H_3PO_4 concentration in aqueous

Figure-2   Schematic Flow Diagram of Nissan C Process
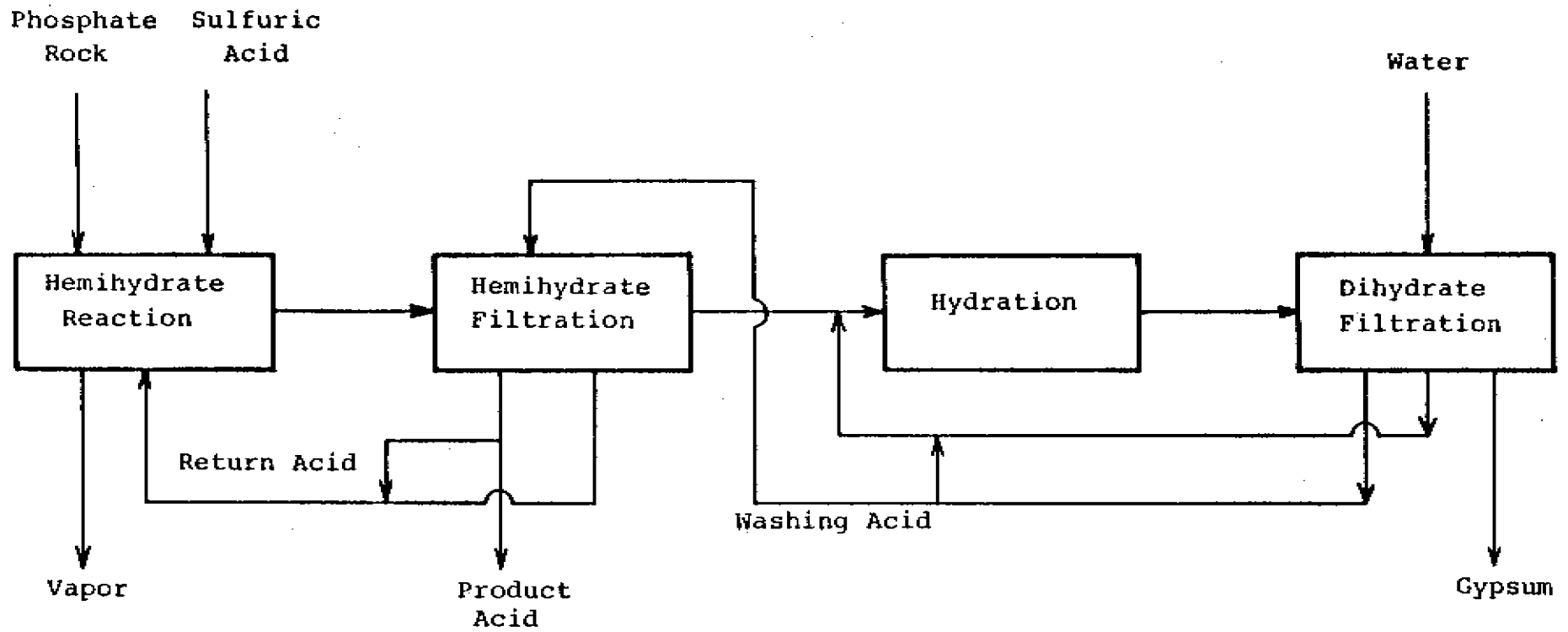
Figure-3 <u>Uranium Concentration on Nissan C Process in the Commercial Plant</u>

Example

Unit : U ppm
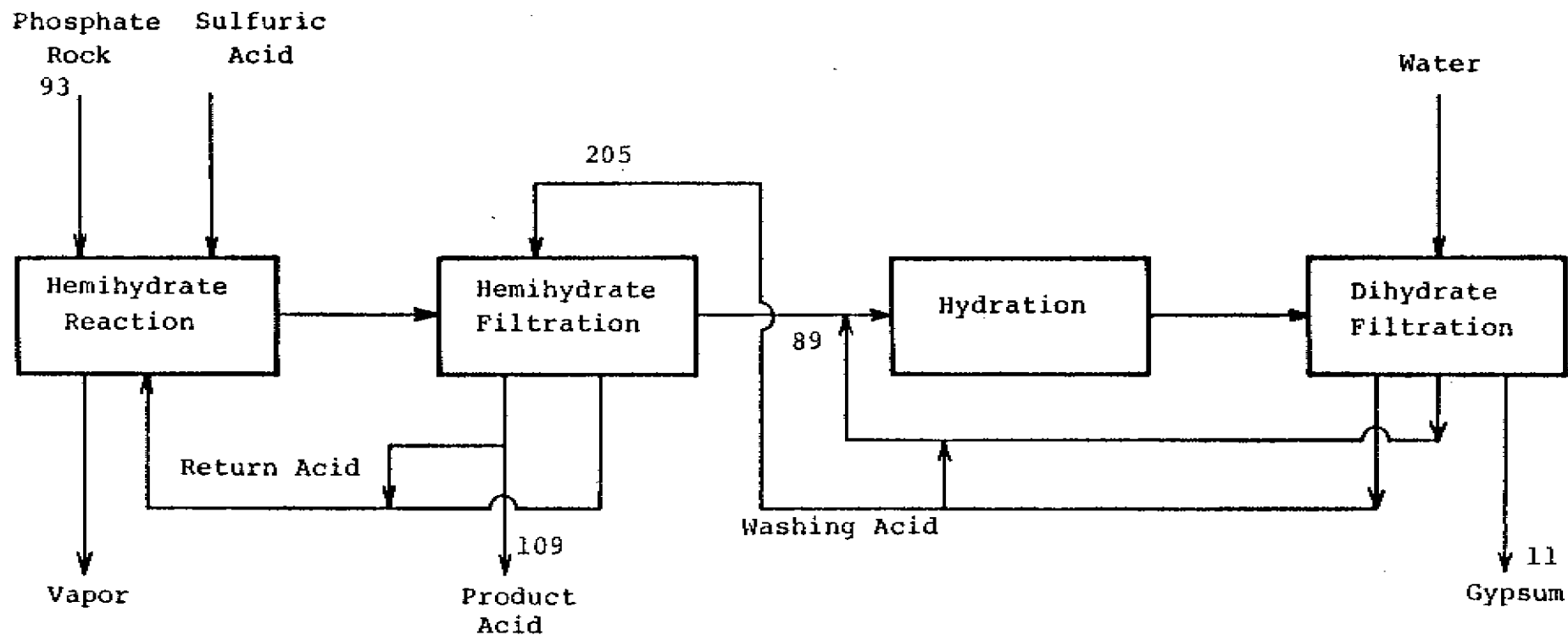
Figure-4   Uranium Concentration Balance on Nissan C Process without Uranium Extraction in the Bench Scale Unit

Example   Unit : U ppm

Phosphate   Sulfuric
Rock   Acid   Water
93

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                                    205
  +--------------+         +--------------+         +--------------+         +--------------+
  | Hemihydrate  | Solid 92| Hemihydrate  |         |              | Solid  9| Dihydrate    |
  | Reaction     |---------| Filtration   |---------|  Hydration   |---------| Filtration   |
  |              | Liq. 111|              |         |              | Liq. 205|              |
  +--------------+         +--------------+         +--------------+         +--------------+
                                    142       157                                112

         Return Acid                      Washing Acid
           130                  111
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Vapor   Product   Gypsum
                   Acid   11
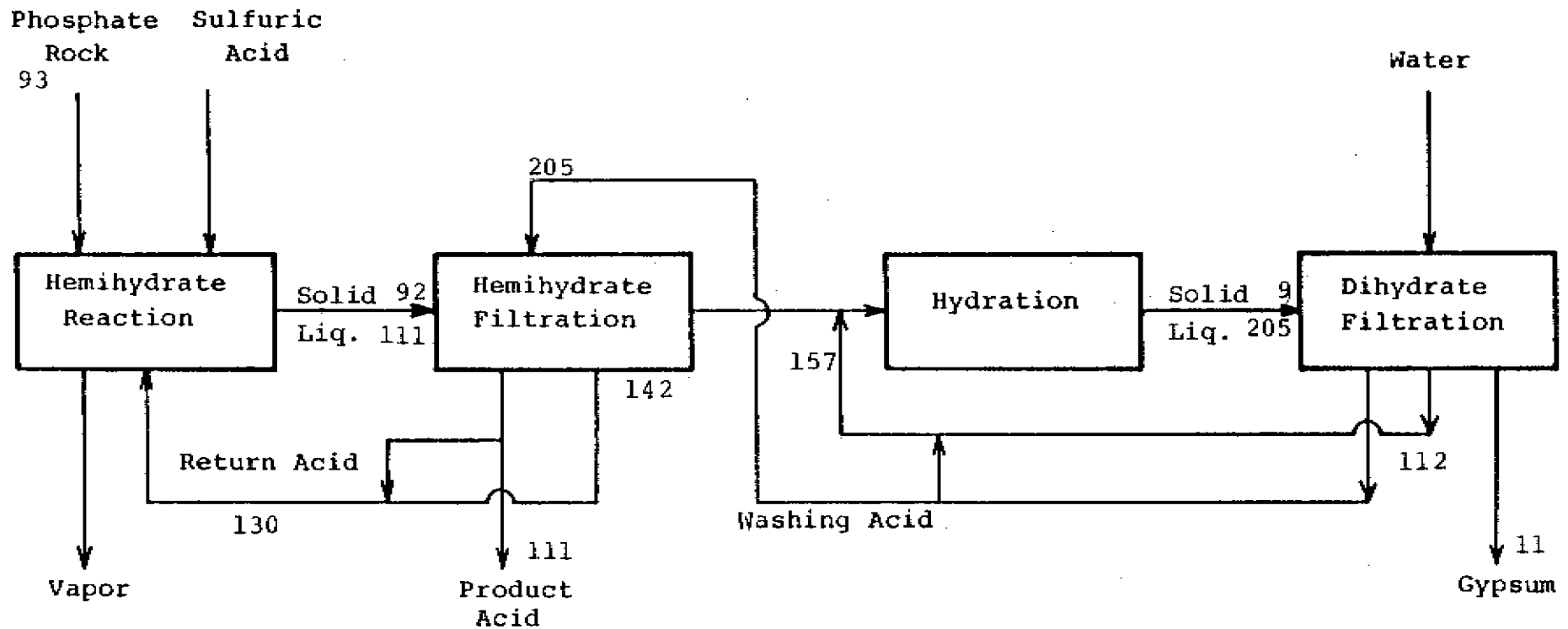
Figure-5   Uranium Concentration Balance on Nissan C Process with Uranium Extraction in
the Bench Scale Unit

Example   Unit : U ppm
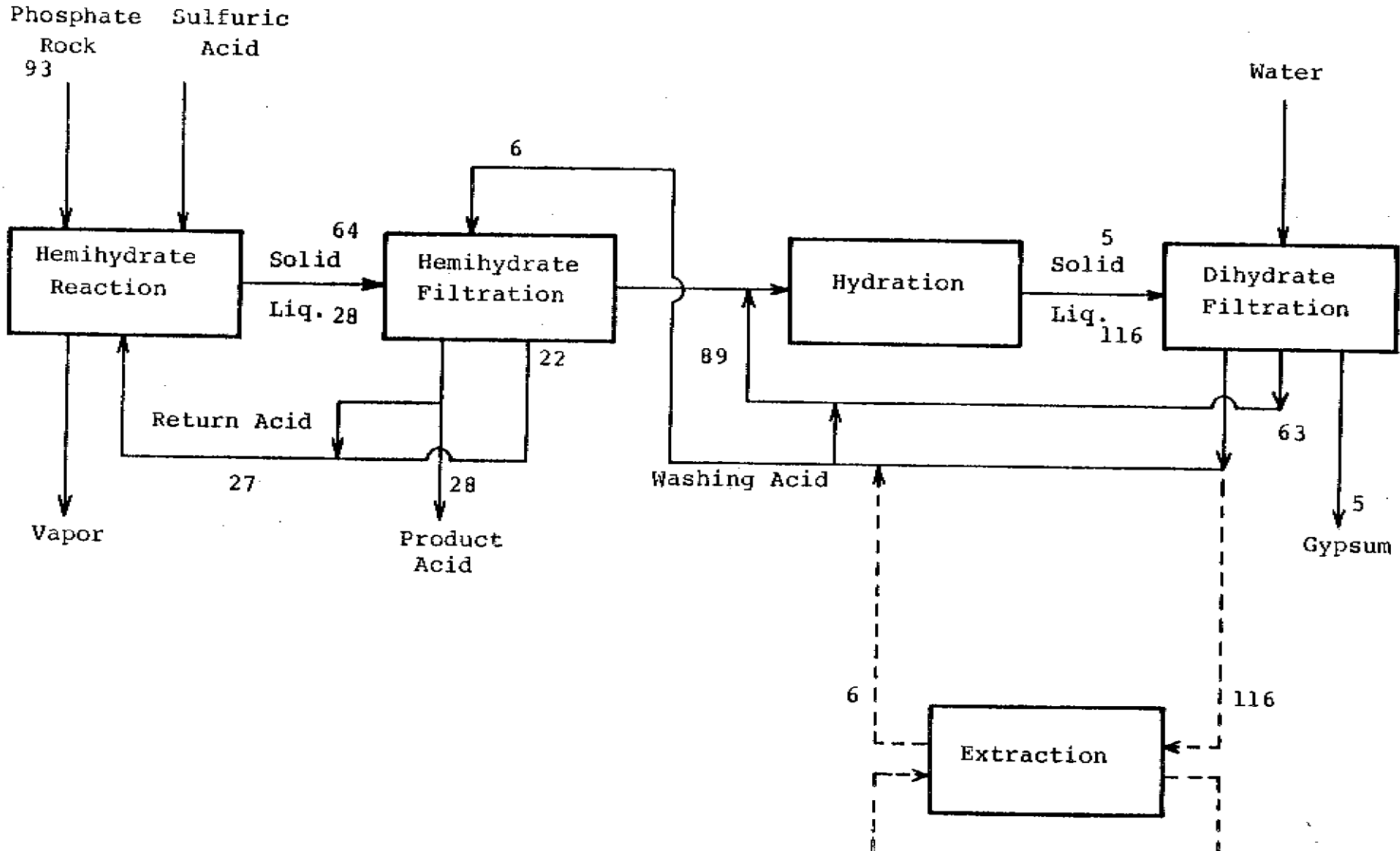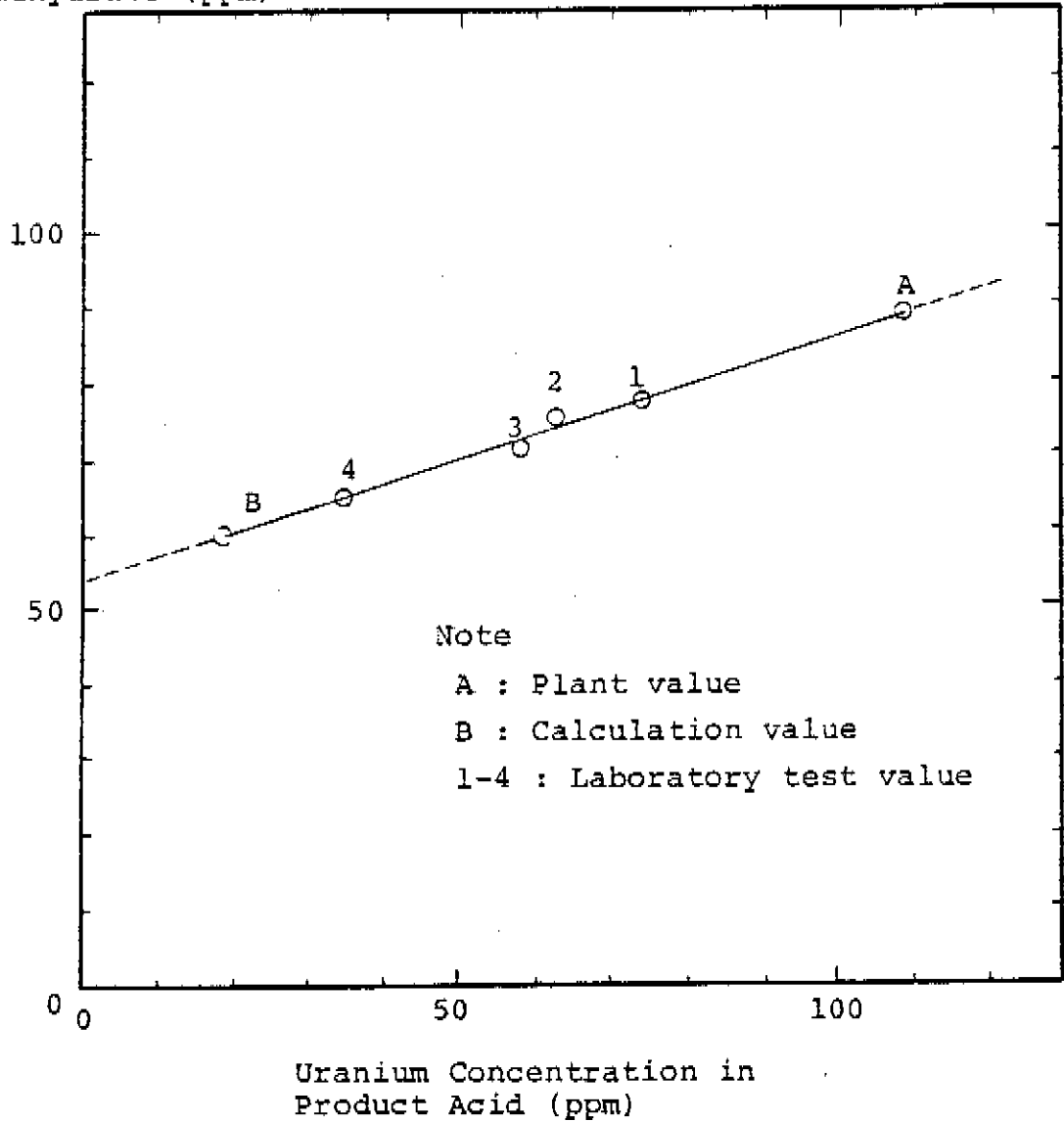
Figure-6   Effect of Uranium Concentration in Phosphoric Acid
            on Uranium Concentration in Calcium Sulfate Hemi-
            Hydrate

Uranium Concentration
in Hemihydrate (ppm)

Uranium Concentration in
Product Acid (ppm)

TA/82/6   Uranium recovery in a hemi-hydrate process of concentrated acid production, by
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DISCUSSION : (Rapporteur Mr. C.H.M. VINKE, Windmill Holland BV, Netherlands)

Q - Mr. J.Th. BOONTJE, UKF, Netherlands

   Have you any idea why the uranium is precipitated with hemihydrate and again dis-
   solves in the dihydrate section?

A - We think "P_2O_5 concentration and oxidation reduction potential of phosphoric acid
   affect the behaviour of uranium".

Q - Mr. G. BELPAIRE, Prayon-Rupel, Belgium

   1. At what temperature is the dihydrate separated by filtration from the acid?

   2. What is then the temperature at which the filtrate is preheated to extract ura-
      nium?

   3. According to the data mentioned in the paper, the rate of solubilization of ura-
      nium is 92%; $\pm$ 80% of uranium is solubilized in the product acid (46.5% P_2O_5):
      as a result the total loss is $\pm$ 100% - (92 x 80%) = 26% compared with 8% in
      the existing conventional processes. Is it not an important handicap?

A - 1. Temperature of dihydrate-slurry for filtration is 60 to 65° C and temperature
      of the filtrate is 55 to 60° C.

   2. The extraction of uranium was done at 50-55° C without preheat.

   3. The uranium in raffinate after uranium extraction in 15% P_2O_5 acid uranium reco-
      very process is recycled to the hemihydrate reaction section. Then the uranium
      is distributed to high concentrated P_2O_5 acid and hemihydrate according to the
      regression formula as shown in our paper. Even if extraction efficiency of ura-
      nium in 15% P_2O_5 acid uranium recovery process is low, overall unrecovered ura-
      nium will be minimized as unrecovered uranium after uranium extraction step is
      recycled in high concentrated P_2O_5 acid production section.

      In addition uranium extraction efficiency from 15% P_2O_5 acid will be much higher
      than the plants commonly recover uranium from 30% P_2O_5 acid, so the total ura-
      nium recovery efficiency at uranium extraction step will be very close to 100%.

      Consequently unrecovered uranium will be about 20% in total of uranium in pro-
      duct acid and that in gypsum, about 12% and 8% of uranium content in phosphate
      rock respectively. Then overall uranium recovery efficiency is expected to be
      close to 80%.

Q - Mr. R.A. DURAND, SCEPC, Morocco

   1. Did you try OPPA as a solvent? Since it is very efficient and not very sensitive
      to P_2O_5 concentration, it should enable to reduce the amount of uranium in phos-
      phoric acid containing 15% P_2O_5 to a few ppm in a few stages.

   2. You showed that uranium extraction did not affect the Nissan phosphoric acid
      process. Did you check if the quality of uranium extracted phosphoric acid did
      not affect the technology and the quality of the downstream production: TSP,
      DAP, MAP, STTP...?

A - 1. We did not test the OPPA system in detail because in our case we have to extract UO_2^{2+} (U + 6) from diluted acid.

2. We have not tested in detail. According to preliminary test and our experience, we think in this stage "there will be little effect in production of TSP, DAP and MAP and there will be a little effect in production of STPP".

Q - Mr. M. GAURON, COFAZ SA, France

1. What is the variation of the uranium distribution in the hemihydrate sector according to the type of phosphate?

2. Did you identify the uranium compound which precipitates in the hemihydrate section?

A - 1. We have done many preliminary tests, for example, Florida, Idaho, North Carolina, Morocco, Jordan, Duchess and mixed rock, and done with Florida rock in detail. Generally uranium in hemihydrate is more than in dihydrate and in hemihydrate section, uranium concentration in hemihydrate is higher when oxidation-reduction potential in acid is lower.

2. We are investigating the reason why uranium is precipitated in hemihydrate.