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THE COMMERCIAL USE OF KOLA PHOSPHATE
IN
NISSAN C-PROCESS (NEW NISSAN PHOSPHORIC ACID PROCESS) PLANT

mitsuya miyamoto/General Manager
masao kubo
Technology Licensing Department
Engineering Division
Nissan Chemical Industries, Ltd.
JAPAN

1. PREFACE

Nissan Chemical Industries, Ltd. has developed a new wet phosphoric acid process (Nissan C-Process) in which highly concentrated phosphoric acid, 45 % P_2O_5 or more, can be produced directly along the route of combination of hemihydrate and dihydrate steps. And Nissan has been running a small unit of commercial scale of 40 MTPD in its Toyama Works since the middle of 1974. A new unit of 100 MTPD P_2O_5 , which was built in Miyako Works of Rasa Industries Co. Ltd. in Japan in 1975, has been running successfully maintaining 45-48 % P_2O_5 of product acid strength and 98 % P_2O_5 recovery for both Florida 72 BPL rock and mixture of Florida 72 BPL, Florida 68 BPL and Jordan 75 BPL rocks.

Nissan has verified in these two plants that successful operation can be attained by the use of various kinds of phosphate rock widely available in the world, including Florida and Morocco.

In May 1977, a commercial scale run was conducted in the plant at our Toyama Works using another world-wide rock, Kola phosphate rock which is from igneous origin. It was verified through this run that the operation of Nissan C-Process can be successfully performed also with Kola rock, equally to or better than Florida or Morocco rock.

The following is a report on the results of this run.

2. PLANT PERFORMANCES AND OPERATION

The commercial run was conducted in the C-Process plant at our Toyama Works using Kola 84 BPL phosphate rock in May, 1977.

The Kola rock was supplied without grinding. Though the operation was once interrupted by the trouble of rock conveying unit which was attributed to the special properties of Kola rock powder, the run was performed satisfactorily in process-wise achieving performances as designed based on the results of bench scale tests for Kola rock.

The start up of the plant was carried out using return acid of 35 % P_2O_5 strength which was produced from the Kola rock prior to the start up. Within a short time after the start, the slurry of hemihydrate and acid (43 % P_2O_5) having good filterability was obtained, and production rate reached soon 30 MTPD P_2O_5 as designed and it was kept through the run.

The strength of product acid was 43-44 % P_2O_5 in the first half of the run and raised to 45-47 % P_2O_5 in the latter half. It is illustrated in Fig-1.

The P_2O_5 recovery was average 97.7 % in the run. The flow diagram of the run is attached hereto, as Fig-2.

Properties of Kola phosphate rock in Nissan C-Process are stated hereunder in comparison with those of Florida or Morocco phosphate rock.

1) Decomposition ratio in hemihydrate stage

Particle size of the Kola rock as delivered was finer than that of Florida or Morocco having been used in the C-Process plants and accordingly the rock was used without grinding. Decomposition ratio in hemihydrate stage was 94 %, the same as that of Florida or Morocco in the same retention time. In Table-1, particle size of the Kola rock and Florida/Morocco rock of feeding to C-Process plant are shown :

[Table-1]

	Kola	Florida/Morocco
- 16 Tyler mesh	- %	100 %
- 48 "	-	65
- 100 "	83	10
- 200 "	52	-

2) Filterability of hemihydrate slurry

Filterability of the hemihydrate slurry obtained in the run was good as expected from the results of bench scale tests conducted in Nissan C-Process using Kola phosphate rock. The surface area of the filter applied in the tests which corresponds to the filterability of 4.0 metric ton P_2O_5/m^2 -effective day was enough to filter the slurry and wash the hemihydrate cake with the washing acid.

The filterability of the hemihydrate slurry derived from Kola phosphate rock is expected to reach 4.5 metric ton P_2O_5/m^2 -effective day or more which is about 30 % higher than that of hemihydrate slurry from Florida or Morocco rock.

Washing efficiency of hemihydrate cake obtained in the run was also good and soluble P_2O_5 remained in the cake after washing was a small amount. Eventually P_2O_5 concentration in liquid phase of dihydrate slurry in hydration stage was maintained between 11 % and 14 % which is favourable to accelerate hydration velocity of hemihydrate to dihydrate.

Hemihydrate crystals obtained in the run, as shown in a photomicrograph (Fig-3), formed agglomerates like Florida or Morocco rock. Good filterability of the hemihydrate slurry derived from Kola phosphate rock is attributed to large size agglomerate of crystals and low viscosity of 1st filtrate.

The specific surface area of hemihydrate crystals obtained in the run was 20-30 % less than that of Florida or Morocco.

The viscosities of phosphoric acid derived from Kola and Florida phosphate rocks were 4.5 centipoise and 9 centipoise respectively under temperature of 75 °C and acid strength of 45 % P_2O_5 .

3) Hydration velocity

Hydration of the hemihydrate obtained in the run to the dihydrate required longer time than any other kind of phosphate rocks, as expected from the results of bench scale tests.

Hydration of the hemihydrate to the dihydrate was completed sufficiently in the run within the designed retention time, since we applied operating conditions as stated below, which accelerate hydration velocity. However it was clarified that hydration of the hemihydrate derived from Kola phosphate rock to the dihydrate still requires twice of more time than that of the hemihydrate derived from Florida phosphate rock.

We have investigated the conditions which would accelerate hydration of the hemihydrate derived from Kola phosphate rock Nissan H-Process, the hemihydrate dihydrate wet phosphoric acid (30 % P_2O_5) process. According to the investigation, low H_2SO_4 concentration, low P_2O_5 concentration and low F concentration as hydrofluoric acid in liquid phase have been found effectual. We have confirmed the above tendency in the hydration stage of Nissan C-Process by bench scale tests and applied these conditions in the commercial run. In the run, low P_2O_5 concentration of 11-14 % was achieved by high efficiency of the hemihydrate cake washing on the filter.

Low H_2SO_4 concentration was also achieved easily by the acid balance itself of the C-Process. That is, the acid in slurry of the hydration stage is filtered on the dihydrate filter and used as washing acid of the hemihydrate filter. Finally it enters into the slurry of the hemihydrate stage. In order to complete decomposition of phosphate rock, a part of raw material sulfuric acid is fed to the hydration stage. Therefore, when the sulfuric acid is reduced so as to take low H_2SO_4 concentration in the hydration stage, sulfuric acid feed to the hemihydrate stage is increased correspondingly to the reduced amount in the hydration stage. Thus, in the C-Process, optimum H_2SO_4 level for decomposition and/or hydration can be taken easily in the hydration stage.

Further, low F concentration in the hydration stage can also be achieved by addition of active SiO_2 , for example diatomaceous earth.

A short discussion on hydration velocity of hemihydrates derived from igneous phosphate rocks is made hereafter in item-3.

4) Crystal form of dihydrate and filterability of dihydrate slurry

Crystals of the dihydrate obtained in the run were long and this rectangular form as foreseen by us from the results of bench scale tests conducted in Nissan C-Process using Kola phosphate rock. They are shown in a photomicrograph in Fig-4.

Such crystal form is so different from that of dihydrate obtained from Florida or Morocco rock in Nissan C-Process, that is, rhombic form. We have experienced such long and thin crystals of dihydrate in Nissan H-Process in case of using igneous phosphate rocks, such as Kola, Tapira (Brazil), Pharaborwa (South Africa) etc. As we anticipated that washing efficiency of such dihydrate cake on the filter would be lower due to high liquid content in it, two stages washing was applied in the run.

Filtration velocity of the dihydrate slurry obtained in the run was similar to that of dihydrate slurry derived from Florida or Morocco. However, required surface area of the filter must be increased by about 25 % corresponding to the additional washing stage.

Moisture content of dihydrate cake ex filter was high (30-35 %) compared to that (20-25 %) derived from Florida or Morocco rock. Accordingly, though less washing efficiency was assumed in each stage of washing, the P_2O_5 loss contained in cake moisture could be reduced to lowest level on the whole washing by applying two stages washing.

5) Final decomposition ratio and P_2O_5 efficiency

The final decomposition ratio in the run was 0.3 % less than that of Florida rock.

The P_2O_5 recovery was average 97.7 % in the run.

6) Other observation in the run

Foaming

Kola phosphate contains less CO_2 and organic matters. Therefore, no foaming was observed and the levels of pump tank and seal tanks did not vary. Eventually it was very easy to achieve and maintain the balance of acid intake and output and to maintain stable and consistent plant operation.

Fluidity of dihydrate slurry

Fluidity of the dihydrate slurry was less smooth than that from Florida or Morocco rock, and so it is necessary to give appropriate consideration on the design of some equipments, for example, emergency electric power supply for agitators of hydration tanks.

Evolution of fluorine

Fluorine contained in Kola phosphate rock evolved in digestion stage to almost the same extent, 35-40 % as that in case of using Florida or Morocco phosphate rock.

7) Chemical analyses of products

The example analyses of product acid and by-product gypsum ex filter are shown as well as that of phosphate rock in Table-2.

[Table-2]

(% on dry basis excepting moisture)

	Phosphate Rock	Product Acid	By-product Gypsum
T-P ₂ O ₅	38.87	46.02	0.52
W-P ₂ O ₅	-	-	0.14
CaO	50.46	0.03	30.70
SO ₃	0.00	1.67	44.85
SrO	2.93	0.00	1.83
F	3.30	1.57	0.47
SiO ₂	1.16	0.49	0.35
MgO	0.09	0.06	0.002
Fe ₂ O ₃	0.29	0.50	0.02
Al ₂ O ₃	0.42	0.23	0.05
Na ₂ O	0.43	0.05	0.10
K ₂ O	0.38	0.04	0.19
Crystalline Water	-	-	19.65
Moisture	1.0	-	32.0

3. HYDRATION VELOCITY OF HEMIHYDRATES FROM IGNEOUS PHOSPHATE ROCKS

Judging from our investigations by bench scale tests, we have assumed that the hydration of the hemihydrate derived from Kola phosphate rock is delayed by SrO which is contained in the rock much more than Florida or Morocco rock.

SrO content in typical phosphate rocks are shown together with other main components in Table-3.

[Table-3]

	Kola	Florida	Morocco	Nauru	Phalaborwa	Tapira
BPL %	84	72	72	84	82	85
P ₂ O ₅	38.87	33.71	33.30	38.58	37.43	39.04
CaO	50.46	48.68	51.76	52.68	51.22	54.16
SrO	2.93	0.11	0.11	0.01	0.83	1.33
F	3.30	4.02	4.12	2.98	2.45	1.75
SiO ₂	1.16	5.16	1.96	0.13	1.96	0.79
Al ₂ O ₃	0.42	0.53	0.45	0.29	0.25	0.16
Fe ₂ O ₃	0.29	1.16	0.17	0.25	0.47	0.75

Kola rock contains particularly high SrO content compared with other rocks and other igneous rocks, Tapira and Phalaborwa, show also high SrO content.

It has not been made clear by what mechanism the delay of hydration of hemihydrate is caused due to high SrO content in phosphate rock, Dr. Murakami, however, hypothesized ¹⁾ on this question as follows :

After he verified by X-ray diffractometry that solid solution of calcium sulfate hemihydrate and strontium sulfate is formed in hemihydrate stage of hemihydrate dihydrate process, in case of using Kola rock, he stated that solubility of the hemihydrate in water or phosphoric acid is decreased and eventually dissolution of such hemihydrate into water or phosphoric acid is delayed owing to:

strontium sulfate having no crystalline water and less solubility enters into crystal lattice of the calcium sulfate hemihydrate.

We have found following tendency towards the delay of hydration of hemihydrates from towards rocks containing much SrO through many investigations by bench scale tests in both Nissan H-Process and C-Process.

(1) Hemihydrate from rock having higher SrO content requires longer hydration time.

- 2) Hydration of hemihydrate from rock having higher SrO content is delayed heavily or inhibited by high H_2SO_4 concentration in phosphoric acid.

This effect is in marked contrast to that in case of hydration of hemihydrate from rock containing less SrO content, i.e., hydration of such hemihydrate is accelerated in a certain range of rather higher H_2SO_4 concentration.²⁾

- 3) Hydration of hemihydrate from phosphate rock containing less F, even if containing much SrO, is completed within not so long retention time in Nissan H-Process.
- 4) Hydration of hemihydrate from rock having high SrO and F contents can be accelerated and completed by maintaining low H_2SO_4 concentration in phosphoric acid and adding active silica to slurry.

It is assumed to be attributed to conversion of hydrofluoric acid into fluorosilicic acid which delays hydration of hemihydrate far less than hydrofluoric acid.

4. CONCLUSION

We verified that Kola phosphate rock can be used satisfactorily in Nissan C-Process, equally to or better than Florida or Morocco rock, through the commercial scale test running.

And the behavior of Kola rock in the plant operation was almost the same as those expected from the results of bench scale tests.

So far the processing of Kola rock and igneous rocks in the route of combination of hemihydrate and dihydrate steps to obtain high concentration acid and has been said to be difficult, now we are confident that igneous type rock as represented by Kola rock can be used satisfactorily in Nissan C-Process.

Fig-1 P₂O₅ Concentration of Product Acid

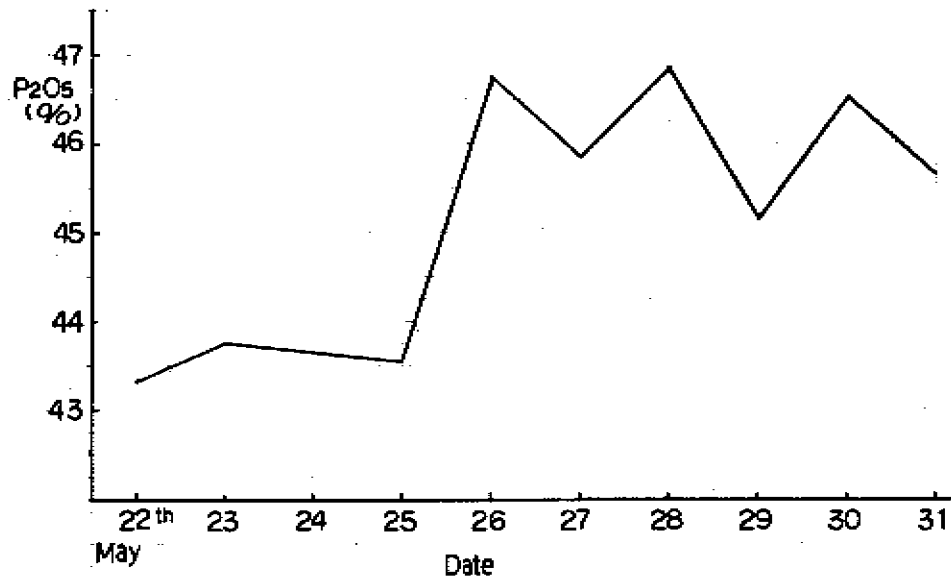
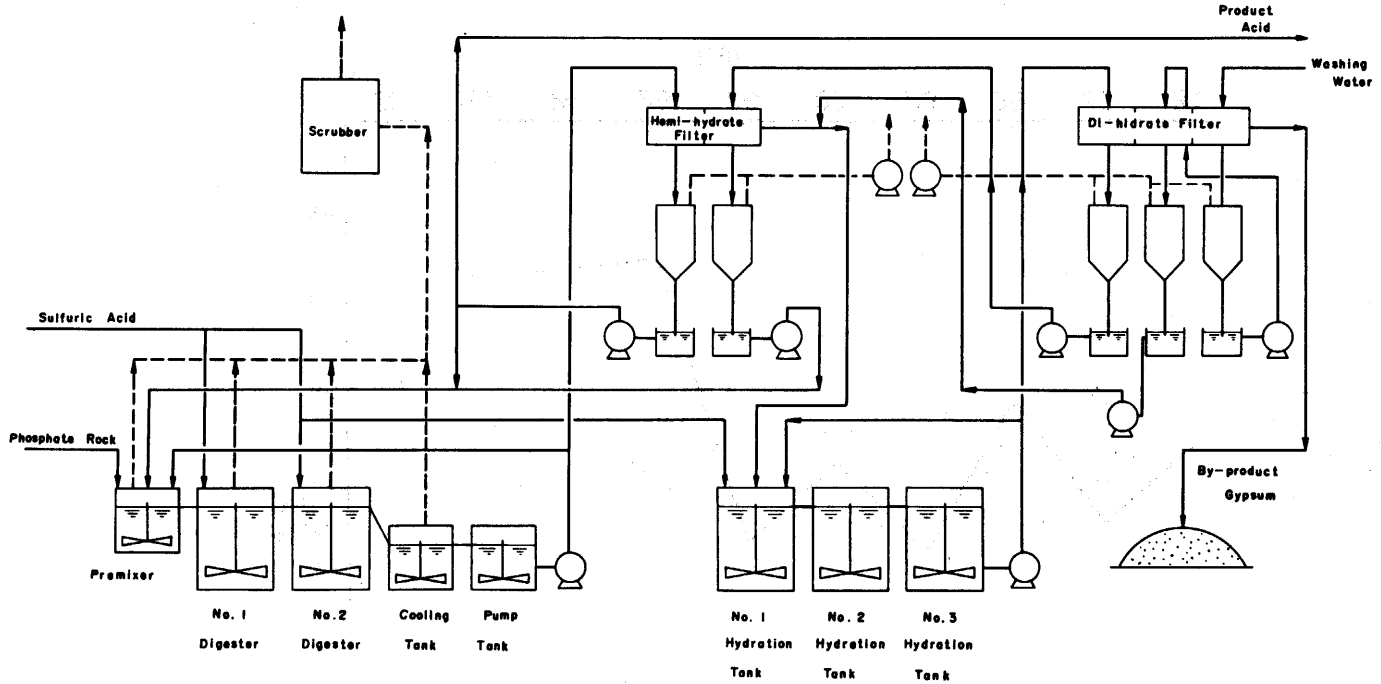


Fig-2 Flow-diagram of Test Run using Kola Phosphate Rock



PHOTOMICROGRAPHS OF CALCIUM SULFATE

Fig-3. Hemihydrate

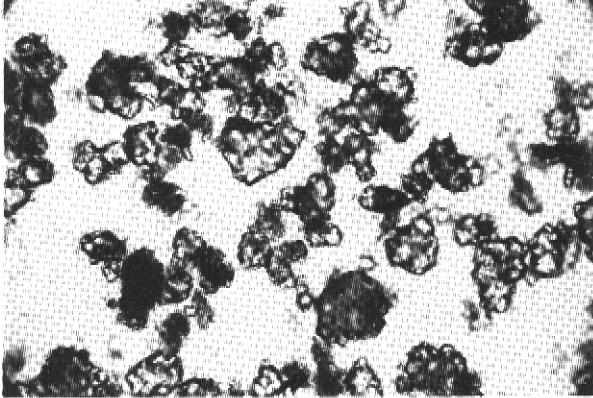
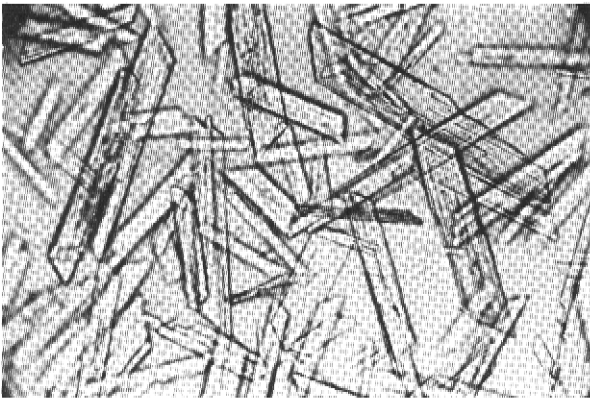


Fig-4. Dihydrate



[References]

- 1) K. Murakami, et al., Some anomalous properties of hemihydrate obtained from Kola phosphate rock, Gypsum & Lime, Japan, NO.84, 163 (1966)
- 2) I. Moriyama, T.Abe, Crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced in the manufacture of phosphoric acid by the wet process. II, The journal of the society of chemical industry, Japan, 66, 1769 (1963).