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HIGH IMPURITY ROCK IN FERTILISER MANUFACTURE - EXPERIENCES WITH UDAIPUR ROCK

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SUMMARY

In India more than half a million tonnes run of mine rockphosphate from Udaipur mines containing high silica and other impurities is used in the manufacture of fertilisers every year. A lot of experience has been gained during last decade by various units in processing the unbeneficiated rock under diverse conditions and Indian industry has optimised the use of this raw material. The use of unbeneficiated rock poses certain technical problems. An attempt has been made to discuss the operational problems which have been encountered in the manufacture of SSP, phosphoric acid and nitrophosphates with Udaipur rock and how these have been solved. Process conditions and experience on the exclusive use of Udaipur rock at RCF-Trombay unit for phosphoric acid manufacture have been described. The effect of various impurities in Udaipur rock in the production of nitrophosphate fertiliser has been enumerated.

Until 1968 the entire requirement of rockphosphate for Indian fertiliser industry was met from imports, from Morocco, Jordan and USA, etc. However, about a decade ago successful exploitation of certain domestic deposits of rockphosphate mainly from Udaipur had been done and an increasing quantity of rock is being supplied to the industry. Out of total requirements of about 2.5 million tonnes of rockphosphate, about 0.6 million tonnes is being produced and used from Jhamar Kotra mines in Udaipur. The strike length extends to 16 km with an average width of 15 meters. The total exploitable reserve at Jhamar Kotra mine is estimated to be over 50 million tonnes out of which about 17 million tonnes is of directly usable grade. The Jhamar Kotra ore is precambrian sedimentary deposits consisting mainly of carbonate apatite that approaches closely the composition of fluorapatite. It consists of interlocking, microscopically coarse crystals with minor amount of occluded quartz grains. Much of the dolomite occurs as uniformly dispersed, interlocking grains in the apatite matrix. The gangue minerals are calcite, dolomite and quartz. As is generally known the coarse crystalline apatite rocks are less reactive than the rocks of sedimentary origin of finer grain.

Mainly run of mine grade containing more than 31% P_2O_5 is presently supplied to the fertiliser industry. The ore overburden ratio has very much increased over the past 10 years and was about 3 million tonnes during 1978-79. Plans to increase the output of phosphate ore to one million tonne per year and to install suitable beneficiation facilities are under way. Sufficient experience has now been gained in using the unbeneficiated Jhamar Kotra phosphate containing high impurities in the production of SSP, phos-acid and nitrophosphates.

Analysis of the Udaipur rock presently used in the production of fertilisers is given below :

P_2O_5	31 - 34%
CaO	48 - 50%
SiO_2	7 - 10%
F	3.0 - 3.9%
CO_2	2.5 - 3.6%
MgO	0.25 - 0.6%
R_2O_3	3.0 - 3.5%
Organic matter	0.25 - 0.5%
Cl	50 - 100 ppm.

The kinetics of the solid-liquid reaction between rock phosphate and mineral acids has been studied. The rate of reaction depends on various factors such as the intrinsic property of rock phosphate and its surface area, acidity of the liquid phase, temperature of the reaction, acid rock ratio, diffusion coefficient of hydrogen ions and degree of coating of unreacted rock by precipitated salts during the reaction etc.

The Udaipur rock being sedimentary in origin containing large quantities of siliceous matter not only creates problems in grinding, also suppresses proper reaction, which is already poor due to low carbonates. Apart from nonuniformity of chemical composition and physical characteristics of the rock, due to high silica content severe problems of erosion arise in the production of fertilisers. The ground Udaipur rock has a bulk density in the range of 1.69 - 1.84 tonnes per cu.m. The Udaipur rock is much harder, hardness factor 6 Mhos.

EXPERIENCE IN THE MANUFACTURE OF SSP

Udaipur rock being hard with excessive silica, grinding of this rock reduces the capacity of the mill and increases the wear and tear of the grinding rollers and plates. In view of the low carbonate content the consumption of sulphuric acid per tonne of P2O5 has been less by about 10% as compared to Jordan rock. As the CaCO3 is comparatively lower than that of Jordan rock, evolution of CO_2 is limited. Consequently the super produced is not porous but hard. The reaction is comparatively better when the fineness is maintained above 90% through 100 mesh. Conversion efficiency around 80% in ex-den super is achieved. The reactivity is poor and it is critical to maintain the acid strength and temperature in a narrow range (66-68% at 62-65°C). To offset the lower reactivity to some extent the mixer paddles were adjusted to obtain better mixing efficiency and the speed of the mixer was reduced so as to increase the retention time of the rock during reaction. The speed of the den belt was also reduced in order to provide more curing time in the den. Better product is obtained at a denning temperature of 115-120°C.

It was found necessary to maintain slightly high percentage of acid on phosphate rock to allow maturing/curing of unreacted phosphate rock in storage. Conversion efficiency to w.s. P_2O_5 increases to 82-84% after about a week's curing time which is low compared to 94-95% with Jordan rock. The R_2O_3 being high, the super has an element of stickiness. High contents of Al and Mg in the rock influenced the super produced, Al retarding the reactivity and Mg causing reversion during storage and also imparting a hygroscopic characteristic. However, no significant reversion has been observed in analysis of superphosphate during curing period of 2 - 3 weeks. Superphosphate produced from Udaipur rock is dark in colour and becomes harder after curing unlike SSP with Jordan rock. It is found better to add some surface reactant material to improve the storage property. The bulk density of super is higher, 1006 kg/cu.m as compared to 900 kg/cu.m from Jordan rock. The optimum rock to super ratio has been found as 0.58-0.60 and acid to super ratio as 0.35-0.36. The rock has pronounced erosion and corrosion effect on various equipment in the plant, resulting into increased maintenance cost.

EFFECT OF IMPURITIES IN UDAIPUR ROCK IN

THE PRODUCTION OF PHOS-ACID

The wet process is very sensitive to the impurities in the phosphate rock. The reactivity of the rock and good filtration characteristics are very important criteria in the process. Laboratory trials conducted by CFL-Vizag indicated lower reactivity of Udaipur rock as compared to Florida rock. Also the filtered gypsum from Udaipur rock was lumpy and hard. Trial runs were conducted in FACT-Alwaye 25 tpd and 100 tpd dihydrate plants. Udaipur rock of fineness 68% passing through 200 mesh produced under optimum conditions 27-30% P_2O_5 acid with 95-96% recovery efficiency. The crystal formation and growth was satisfactory. The average LxB ratio of most of the crystals was observed to be 10:1. Crystals were found broken at excess SO_3 levels of above 40 g/l and below 25g/l. The filterability of gypsum slurry was 3.3 - 3.8 tonnes P_2O_5 per sq.m. of filter area per day.

GSFC-Baroda carried out extensive test runs with Udaipur rock and its blends with Florida, Morocco and Senegal rocks in different proportions in their 165 tpd dihydrate plant. It was reported that reactivity of Udaipur rock was good and average extraction efficiency of more than 95% was obtained. Consumption of sulphuric acid with Udaipur rock was less by about 4% per tonne of P_2O_5 as compared to other rocks. Defoaming agent (Oleic acid) was not required because of low organic matter and CO_2 content. Due to low chloride content, the life of the mild steel rubber lined equipment like agitators, pumps was quite high. The major problem encountered was reduction in plant capacity due to poor crystallisation of gypsum in reactors. Lots of attempts were made to improve the crystal structure and size by changing the various parameters like slurry density and SO_3 control but the crystals could not be improved. The gypsum contained 2-3% P_2O_5 on dry basis and this could not be used for the production of ammonium sulphate. The filter cloths had to be changed more frequently because of coprecipitation of silica on the filter cloth which hampered the filtration rates. Excessive precipitation of silica in pipelines, vessels and equipment caused frequent shutdowns. Moisture about 30% in gypsum was also high which upset the water balance in ammonium sulphate plant. Because of the problems experienced with Udaipur phosphate, GSFC plant decided to use blends of 1:1 with Morocco, Florida or Senegal rocks and found 1:1 blend of Udaipur and Senegal rock as most suitable for their plant.

OPERATIONAL EXPERIENCE WITH UDAIPUR ROCK

Udaipur phosphate is being used in a 100 tpd P_2O_5 phos-acid plant based on Nissan hemi-hydrate- dihydrate process at RFC-Trombay. The experience gained is briefly described.

GRINDING

Having more silica percentage (7-10%) as against Jordan rock (3-4%) that too quartz type, ball mill capacity has gone down by one third. Being abrasive, erosion of equipment, ducts, plates, and pipings is very fast. The power consumption for grinding is 6-7 Kwh higher per tonne of rock due to hardness of the rock.

REACTION AND CRYSTALLISATION

Reaction with Udaipur rock at initial stage is faster than Jordan rock. Temperature rises upto 100°C at full load against 85-90°C in Jordan rock in premixer and 105°C in digestor. The reactivity of Udaipur rock (98-98.5%) is slightly lower as compared to Jordan rock (98.5-99%). Stable hemi-hydrate may form at the digestor temperature which does not hydrate fully and could blind the filter cloth during filtration if proper operational vigilance is not kept. Since the organic matter is very low in the Udaipur phosphate, no anti-foaming agent is required to be added.

The $CaO:P_2O_5$ mole ratio in the indigenous rock is lower (3.56) than in Jordan (3.80). Due to lower CaO/P_2O_5 ratio, the sulphuric acid consumption per mole of P_2O_5 is lower with Udaipur rock. However, in order to have better gypsum crystals, slightly higher quantities (i.e. 4-4.5%) of sulphuric acid is needed as free acid in the phosphoric acid derived from Udaipur rock as compared to Jordan rock (free acid 3.5%). Hence ultimately the effect of low CaO content is practically neutralised in order to grow better crystals of gypsum, by way of using 2-3% more sulphuric acid on the total consumption of acid.

The adverse effect of higher silica on gypsum crystal growth has not been established. The silica is in the form of alpha silica which aggravates the erosion/corrosion problems.

In crystallizer, the temperature tends to go beyond the specified temperature of 65°C for hydration, upto 70-72°C. So transformation of hemi-hydrate crystal into dihydrate crystal could be hampered. The crystals from Udaipur rock are comparatively smaller (LxB = 54 μ x 19 μ) whereas the crystal size with Jordan rock is 308 μ x 48 μ. Hydration time for Udaipur rock requires about 10 hours.

The process conditions using Udaipur rock are given below :

Process equipment	Temperature °C	Decomposition %	Hydration ratio	Residence time (Mint)
Premixer	95-90	60.0	-	4
Digester I	90-95	80.0	-	25
Digester II	90-95	95.0	0.54	25
Hydration Tank I	68-65	-	-	360
Hydration Tank II	65-60	-	-	360
Hydration Tank III	60-55	98.0	1.9 -1.93	360

FILTRATION

Filterability is good but solid content is more in 30% acid (1.5-1.7% solids). In 50% acid solid content is 2.5-2.7%. Within 10 days filtrate compartment becomes full of gypsum and chokes the seal leg. Once seal leg is chocked, the carry over of 30%, 12% and 4% acid starts and loss of P_2O_5 in gypsum increases. Therefore, cleaning of filtrate compartment every 10th day becomes necessary.

CONCENTRATION

As the solid content in the 30% and 50% acid is relatively more, the connected pipe lines and heat exchanger tubes get choked frequently. Every 15th day, heater tube cleaning is required, and the product acid lines are required to be flushed every week.

The raw material and utility consumption for phos-acid (50% P_2O_5) with Udaipur rock is as follows :

Raw material/utility	Quantity per t P_2O_5
Rock (34% P_2O_5), t	3.0
Sulphuric acid, t	3.0
Steam, t	2.67
Water, M^3	42.0
Power, KwH	360.0

A typical analysis of gypsum obtained from Udaipur rock is given below :

CaO	30.09%
Total P_2O_5	0.53%
W.S. P_2O_5	0.11%
F	0.56%
Free moisture	19.50%
Combined moisture	19.2%

UDAIPUR ROCK IN

NITROPHOSPHATE PRODUCTION

In the RCF-Trombay nitrophosphate (45000 P_2O_5 tpy capacity) plant Udaipur rock is acidulated with nitric acid to produce nitrophosphates (20:20 and 15:15:15). The citrate insoluble P_2O_5 in the fertiliser is less than 1% which indicates the reactivity of the rock is 99 per cent.

The Udaipur rock being harder, the power consumption for grinding is higher. When ground to a fineness of 60% through 200 mesh the rock is dense and with high specific gravity, this brings up problem of flow from the feed hoppers and the various chutes, especially during the rainy season when moisture is also high at 6-8% and with the normal drying furnaces which are designed for moisture input of not more than 2% moisture cannot be evaporated fully. There are failures on the grinding mill machinery and its associated duction, hoppers cyclones and hence more maintenance costs. In addition, the capacity of grinding equipment is reduced by 33%.

Silica upto 4% is adequate to react with the fluorine part of the rock. Higher silica content of the rock affects the life of the various running equipment such as pumps, glad packing, stainless steel reactors, stainless steel agitators and there are frequent failures of the various parts due to erosion.

The magnesium content of the rock normally varies from 0.25 to 0.35% but sometimes when it is more, it creates problem of high viscosity in the ammoniated slurries under alkaline conditions resulting in problems on the flowing characteristics of the slurry. This is, however, controlled by increasing the water content of the slurry and the temperature conditions but it affects the productivity from the dryers/granulators.

The chloride in Udaipur rock being very low, lower than 100 ppm, the problem of corrosion on stainless steel 316L used for the reactors for acidulation and ammoniation vessels has been considerably reduced. The rock has very low organic matter and hence there is no problem of foaming and frothing and no anti-foaming agent is required. Due to low organic matter, there is no decomposition of nitric acid to NO_x, thereby reducing the consumption of costly nitrogen bearing nitric acid. Trombay had once used the calcined Moroccan rock and due to high organic matter the additionnal consumption of nitric acid due to decomposition during rock acidulation stage ranges from 7 to 10 kg of nitric acid per tonne of NPK 15-15-15.

Another study with Udaipur phosphate has been carried out by FPDIL, Sindri, in their 5 tpd pilot plant to produce a product 26-14-0 utilising the sulphate recycle process. The HNO_3:CaO mole ratio was 2 during acidulation at 60°C. The reaction time was 60 minutes with this rock to attain a 99% P_2O_5 availability. The reaction time was a little higher than with the other rocks. Due to the presence of higher silica and its peculiar structure, the problem of gypsum precipitation was encountered during the precipitation stage using ammonium sulphate. However, this problem was reduced by settling silica after acidulation. The gypsum cake, containing 0.16% P_2O_5 and 0.13% F on dry basis, was similar to that obtained in dihydrate process for wet process phos-acid. The product contained 15.7% P_2O_5 and 27% N.

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TA/80/3 High impurity rock in fertiliser manufacture - Experiences with Udaipur rock by B.K. Jain, FAI, India

DISCUSSION : (Rapporteur F. Thirion, Société Industrielle de Prayon, Belgium).

Questions

Mr. P. MORAILLON, Générale des Engrais, France

1) What type of mixer and den do you use in the manufacture of superphosphate and what is the retention time in the den?

2) Is it necessary to grind Udaipur phosphate for the nitric reaction?

Mr. P. BECKER, COFAZ, France

What is the duration of a filtration cycle when you indicate filtration rates of 3.3-3.8 tons P_2O_5/m^2/day?

Mr. M. BARLOY, CERMI, France

On page 3-4, you state: "The adverse effect of higher silica on gypsum crystal growth had not been established". How do you explain the unfavourable influence of silica on crystal growth?

Summary of answers

We can state that we come across the constraints associated with low grade rocks. When processing Udaipur phosphate, we do not understand why silica has a detrimental effect on gypsum crystal growth while, for some authors, silica has a favourable effect. The results on gypsum filtration are similar to those obtained with Jordan phosphate.

Phosphate rock must be ground for all usage but it is even more important in single superphosphate and phosphoric acid manufacture.

In the manufacture of superphosphate, the retention time in the den is 40 min. and we use a Kuhlmann mixer.

We had important losses due to a very thorough grinding and to blocking of the turbines due to phosphate particles 300 mesh.