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U.S.S.R.

The Progress of Hydrothermal Processing

of Phosphate Rock

50 years ago an Estonian chemist, Jaak Kuusk, established
that calcinating phosphorite in a laboratory gas furnace
at 1400°C a transition of phosphorite to a citric-soluble
form takes place, i.e. phosphorite becomes assimilative
for plants as a phosphate fertilizer. Jaak Kuusk assumed
that the decomposition of the phosphate mineral of phos-
phate rock takes place on account of its interaction with
quartz, contained in rock, not considering the influence
of water vapour formed in the burning of gas. The results
of his work he published in 1930 in the Transactions of
the Tartu University /1/.

The work of Jaak Kuusk attracted the attention of inves-
tigators in the U.S.S.R.as well as in the U.S.A.and other

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countries, who continuing and developing his experiments
showed that it wasn't quartz but water vapour that played
the main role in the decomposition of fluor-apatite. Thus
a new method of processing phosphate rock was created,
which was called the hydrothermal method.

First this method was applied in industry in the U.S.A.
during World War II according to two variants - in the
solid phase in rotary furnaces and by means of melting the
rock in a shaft furnace /2,3/. At present also fluidized
bed furnaces are used for this process /4/.

The process of hydrothermal treatment of phosphate rock
was investigated in the U.S.S.R.from the fiftieths especi-
ally at the Scientific Institute on Fertilizers and Insec-
tofungicides. The practical outcome of these investigations
was the introduction of this process into industry on the
basis of the solid variant,treating the concentrate of
Kola apatite in a rotary furnace (in 1959), as well as on
the basis of melting the Karatau phosphorite in a cyclone
furnace (in 1963). Experiments of hydrothermal treatment
of phosphate rock on pilot plant installations in a flui-
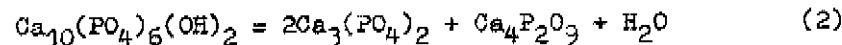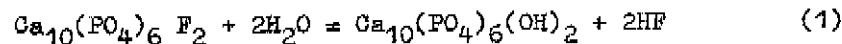dized bed furnace have also been carried out.

In the U.S.S.R.at the present time the hydrothermal proces-
sing of natural phosphates is put into practice in four
plants, which produce over a million tons a year of defluo-
rinated phosphate. The latter is used chiefly as a phospha-
tic feed supplement in cattlebreeding (provided the phos-
phate dissolves in a 0.4% solution of hydrochloric acid
and contains no more than 0.1-0.2% fluorine). As defluori-
nated phosphate is much cheaper in comparison with other
kinds of phosphate feed supplements, obtained on the basis
of phosphoric acid, so further development of its producti-
on is envisaged. The object is to produce part of the pro-
duct in the form of citrate or citric-soluble phosphate
fertilizer. The effectiveness of the latter is well dis-
played in various agricultural conditions with numerous

vegetative and field experiments on various kinds of soil.

Results of the first work, carried out in the U.S.S.R. are generalized in the monograph published in 1964 /5/. In the period of 1964-1977 more than 50 scientific and technical articles have been published in soviet periodicals only on the chemistry and technology of defluorinated phosphates. Besides, this problem is dealt with in detail in two collected articles /6,7/. Thus, a scientific base is established in the U.S.S.R. and industrial experience in hydrothermal processing of phosphate rock is obtained.

It is impossible to consider all the aspects of this process in this paper. Most attention is paid to some theoretical questions, to the application of various kinds of phosphate rock, and the intensification of the process in carrying it out in the solid phase.

The chemism of the process of the hydrothermal treatment of phosphate rock consests in the proceeding of the following reactions:

$$Ca_{10}(PO_4)_6 F_2 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 2HF \qquad (1)$$

$$Ca_{10}(PO_4)_6(OH)_2 = 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O \qquad (2)$$

Reaction (1) consists in the isomorphous replacement of the fluoride ion the crystal lattice of apatite with a hydroxide ion and reaction (2) in the decomposition of the unstable, in these conditions, hydroxyapatite with the formation of tri- and tetracalciumphosphate. As it is known $Ca_3(PO_4)_2$ exists in several modifications. With the object of averting the transition of the more soluble α – modification of $Ca_3(PO_4)_2$ to the less soluble β-modification (the temperature of the transition is $1100-1200^{\circ}C$) a rapid chilling of the hot product is necessary.

In the presence of admixtures in phosphate rock the che-

mism of the process becomes rather complicated. For ins-
tance, in the presence of quartz phases of transitional
composition are formed on the basis of tricalciumphosphate
and silicophosphates of calcium. In a general form the pre-
sent reaction may be described with the following equation:

$$nCa_{10}(PO_4)_6(OH)_2 + mSiO_2 = 10n\ CaO \cdot 3nP_2O_5 \cdot mSiO_2 + H_2O \quad (3)$$

As a result of this interaction the decomposition of fluor-
apatite proceeds at a lower temperature and a greater rate,
and the product shows greater solubility, because the pha-
ses on the basis of silicophosphates of calcium are well
soluble in citrate solutions. On the other hand, as shown
by the works of I.Ando /8/, in the presence of even small
quantities of Al_2O_3, Fe_2O_3 and MgO the temperature of the
transition $\beta-Ca_3(PO_4)_2$ in $\alpha-Ca_3(PO_4)_2$ increases to
$1250-1450^\circ C$, resulting from this $\alpha-Ca_3(PO_4)_2$ may not be
formed altogether in the process of hydrothermal treatment,
and the product can have low solubility in the standard
solution of citric acid.

Besides chemical and structural changes an important role
is played by diffusion phenomena, conditions of phase con-
tacts, heat exhange etc. in the proceeding of the hydro-
thermal treatment of phosphate rock.

The choice of methods in hydrothermal processing phosphate
rock (in solid or liquid phase) depends on their melting
temperature. Concentrates of Kola apatite, as the purest
raw material containing 39.5% P_2O_5, melts (adding 2% SiO_2)
at $1520-1580^\circ C$. Phosphorites are lower melting and gene-
rally pass over to the liquid phase in a wider range of
temperatures. For instance, in heating some varieties of
phosphorites of the Karatau and Egorov deposits the com-
mencement of the liquid phase can be noticed already at
$1150-1200^\circ C$, and transition into the liquid-molten state
is completed at $1390-1400^\circ C$. Estonian phosphorites occupy

an intermediate position in thermostability, for which the same temperature range is suitable, accordingly, 1380-1430 and 1480-1530°C.

It is advisable to carry out the hydrothermal treatment of phosphates, melting at high temperature, in the solid phase and phosporites, melting at low temperatures, in the molten state. Correspondingly the industry of the U.S.S.R. was the first to start hydrothermal treatment of the concentrates of Kola apatite (with the addition of 2-2.5% sand) at 1420-1470°C in a rotary furnace, and the Karatau phosphorite at 1450-1500° in a cyclone furnace. The first raw material, in conducting experiments on a pilot plant installation in a fluidized bed furnace, was Estonian phosphorite.

In the application of the process certain difficulties have arisen. In the solid phase process the main difficulty was that the temperature of the process was close to the temperature of melting of the raw material, and at the smallest deviation of the parameters of the process from the optimum ones, melting of the phosphate, formation of agglomerates etc. took place, which led to the destruction of the process and stoppage of the unit for cleaning. Therefore additives were being looked for which, added to the phosphate rock, would increase the interval between the temperatures of melting and defluorination of the raw material, thus leading to the stabilization of the process. On the other hand measures were being taken to improve checking and control of the process.

From amongst various tested additives the most effective proved to be phosphoric acid. Addition of this additive (in a definite quantity depending on the kind of raw material) not only increases the thermostability of phosphate rock, but, which is particularly important, brings down the temperature of the process and accelerates the evolution of fluorine.

To begin with, phosphoric acid was being used (instead of quartz) in processing Kola apatite concentrates in a quantity up to 4.5% (evaluated in P_2O_5) from the mass of the latter. As far as granulation of the raw material was also being mastered, so phosphoric acid was added to apatite in the stage of granulation, where it served also as a binding material. Several effects were achieved as a result: stabilization of the process, productivity increase of the rotary furnace approximately by 20%, lowering the temperature of the process by 100-150°C, bringing down dust elimination and expenditure of fuel, increase of the quality of the product from 38 to 41% P_2O_5, soluble in a 0.4% solution of hydrochloric acid /9/. The application of higher doses of phosphoric acid are not advisable, not only because of economic reasons, but because in this case a decrease of thermostability of the phosphate takes place and a loss of P_2O_5 in the gaseous phase is noticed.

Difficulties, shown above, appeared to a greater extent in experimental trials of processes using low-melting poor phosphorites than in hydrothermal processing of Kola apatite. Therefore, research and experimental work was carried out to determine the possibilities and optimal conditions for the hydrothermal processing of those in the solid phase. Besides an object was set to concentrate the product to a considerable extent with P_2O_5 by means of introducing into the process a larger quantity of phosphoric acid.

Resulting from investigations, carried out with phosphorite from the deposit Maardu (Estonian S.S.R.), it has been established that in a fluidized bed furnace a stable regime is achieved with the addition of phosphoric acid in a quantity of 8% (evaluated in P_2O_5), which decreases the weight relations $CaO:P_2O_5$ from 1.44-1.48 in the raw material to 1.1 in the mixture. The process takes place at the temperature 1250-1270°C, which is roughly by 100° lower of the temperature when phosphorite starts deformation. With this procedure phosphorite containing 26-27% P_2O_5

gave a product with an average content of 0.13% F and
32% P_2O_5, soluble in a 0.4% hydrochloric acid. The appli-
cation of a fluidized bed furnace enabled to intensify the
process considerably and to carry it out with a lesser ex-
penditure of fuel.

Phosphorites from the Karatau and Egorov deposits as lower-
melting and with a larger content of impurities (besides,
in a variable quantity) are a more complicated object for
solid phase hydrothermal treatment. However, as a result
of great experimental work with the use of mathematical
methods in planning experiments and processing data, it
was possible to establish the quantitative dependences bet-
ween melting temperatures and composition of mixtures, bet-
ween principal parameters of the process of defluorination,
and to work out optimal regimes of processing. Industrial
testing in a 100 m rotary furnace have confirmed the re-
sults of laboratory experiments. In processing Karatau
phosphorite, containing 25.5% P_2O_5, 42.3% CaO, 3.3% MgO,
13.5% SiO_2, 2.5% F, the optimal dose of acid (evaluated in
P_2O_5) made up 6.5-7.0%, and in processing Egorov phospho-
rite with the content 21.5% P_2O_5, 32.1% CaO, 9.5% R_2O_3,
17.0% SiO_2 and 2.4% F - 10 - 11% of the mass of phosphori-
te. In this case, at the temperature regime providing
1050^0 on the 50-th meter of furnace and in the hot zone of
it 1250^0C, it is possible to carry out the defluorination
process without the formation of a molten phase. The de-
fluorinated phosphate obtained, accordingly contained 36%
and 32% P_2O_5 soluble in 0.4% hydrochloric acid and the
weight relations $CaO:P_2O_5$ in those are about 1.3 and 1.0.

The effect of adding phosphoric acid in processing of apa-
tite concentrates was accounted for by the decomposition
of the impurity-nepheline contained in the raw material
and the interaction of active silica, formed in this reac-
tion, with apatite. To investigate this process more deep-
ly it was decided to study the chemism of the process with
the application of methods of thermal analysis, chromato-

graphy, spectroscopy etc. It was shown that the chemism
of the process is rather complicated and greatly dependab-
le on the composition and structure of phosphate rock.

When phosphates are mixed with acid, then reactions with
the formation of monocalciumphosphate occur:

$$Ca_{10}(PO_4)_6 \ F_2 + 14H_3PO_4 + 10H_2O = 10Ca(H_2PO_4)_2 \cdot H_2O + 2HF \ (4)$$
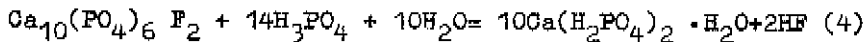
When the obtained mixture is heated, then a multi-stage
dehydration proceeds. In the mixture with phosphorite the
products of dehydration start reaction with the phosphate
mineral already at $300-400^{\circ}C$. This interaction is accele-
rated with the increase of temperature and is completed at
$900-1000^{\circ}C$:

$$Ca_{10}(PO_4)_6 \ F_2 + /Ca(PO_3)_2/_4 + H_2O = 7Ca_2P_2O_7 + 2HF \ ^* \quad (5)$$
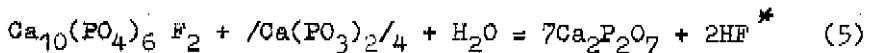
With the increase of temperature above 1000° the rest of
the phosphate mineral reacts with $Ca_2P_2O_7$:

$$Ca_{10}(PO_4)_6 \ F_2 + Ca_2P_2O_7 + H_2O = 4Ca_3(PO_4)_2 + 2HF \quad (6)$$
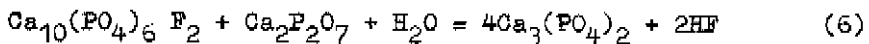
Impurities of magnesium, iron, aluminium, silicon etc.
present in phosphorites considerably complicate the che-
mism of the process.

Thus, the condensed phosphates of calcium, formed in ther-
mal dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$, react with the phos-
phate mineral of the phosphorites at considerably lower
temperatures than processing phosphate by means of only
water vapour and silica. Fluorine passes over principally
in the form HF and SiF_4, and losses of phosphores do not
exceed 1% of its quantity introduced by phosphoric acid.

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* $/Ca(PO_3)_2/_4$ in this equation a highmolecular poly-
phosphate of calcium is represented

Heating mixtures on the basis of Kola apatite no interac-
tion of apatite with the products of thermal dehydration
of $Ca(H_2PO_4)_2$. H_2O up to 500–600° occurs on account of
its lower reactivity in comparison with phosphorite. De-
hydration of the main part of $Ca(H_2PO_4)_2$. H_2O comes to the
end with the formation of a highmolecular polyphosphate
of calcium, which with further increase of temperature re-
acts with apatite rather slowly. Therefore, with rapid hea-
ting it is partly preserved in the mixture, at 960–970° it
melts, and then with the increase of temperature above
1100° decomposes with P_2O_5 passing over to the gaseous pha-
se. Because of the last-mentioned phenomenon it is not ad-
visable too much to increase the norm of phosphoric acid
in processing apatite.

Phosphate in the products of phosphoric-acid thermal pro-
cessing of natural phosphates is represented, principally,
depending on the quantity of introduced phosphoric acid,
maximum temperature height of the process, and content of
impurities in the raw material, by α – and ß-modifications
$Ca_3(PO_4)_2$ and $Ca_2P_2O_7$. The formation of ß-$Ca_2P_2O_7$ in the
product should be avoided (on account of its low solubility
even in a 0.4% hydrochloric acid) by carrying out the
process at a temperature not lower than 1200°C. α –$Ca_3(PO_4)_2$
is rarely formed in the products of this process, there-
fore defluorinated phosphates obtained dissolve only partly
in standard citric acid solutions. For getting phosphate
fertilizers by the use of this method it is required to
introduce into the reaction mixture soda or some other
alkaline or silicate reagent.

In recent years in the U.S.S.R. research work was being
carried on in processing apatite concentrates from the la-
tely started exploitation of Kovdor iron ore deposits con-
taining apatite. The latter is distinguished from Kola apa-
tite by a smaller content of fluorine (as its phosphate
mineral is represented by hydroxyfluorapatite) and a larger
content of impurities principally forsterite, calcite and

dolomite. Resulting from this work processing that raw
material in rotary furnaces at temperatures 1350-1400°C
was put in practice. Besides, phosphoric acid is added in
a quantity of 5.5 % (evaluated in P_2O_5) from the mass of
the concentrate, containing 36 % P_2O_5, 51 % CaO, 2.5-5.0 %
MgO, up to 1.5 % SiO_2, and 1.0 % F. The product containes
41 % P_2O_5 soluble in 0.4 % hydrochloric acid and up to
0.18 % F. Owing to a rational ratio $MgO:SiO_2$ in some kinds
of Kovdor concentrates citric soluble fertilizers can be
obtained from those.

In figures 1 and 2 technological schemes of the two vari-
ants of hydrothermal processing of natural rock, used at
present in industry, are represented. In the table princi-
pal technical indices of both variants are given. On the
basis of waste fluoric gases technical sodium or calcium
fluoride is worked out, which may serve as a semi-product
in the production of fluorine hydride and other compounds
of fluorine. The heat of vaste gases from the furnace is
used in boiler for producing vapour.

<center>Technical indices of the production
of defluorinated phosphates</center>

Indices	Rotary furnaces	Cyclone furnaces
Sizes of furnace,m	l=100, d=3.6	h=2.8, d=1.6
Productivity of product, t/hr	6 - 7	6 - 6.5
Expenditure of standard fuel,kg/t	480	420
Expenditure of electric power,kwhr/t	280	250
Production of vapour, t/t	2	3 - 4

According to standards in force in the U.S.S.R. on phospha-
tic feed supplement the weight relation F:P does not exceed
1:100, and the content of lead makes up no more than 20 g,
no more arsenic than 2g on a ton of product. Defluorinated
phosphate from Kola and Kovdor apatite concentrates contain
no less than 41%, and from Karatau phosphorite - 30±2%
P_2O_5 soluble in 0.4% hydrochloric acid. In the latter, in
conditions of rapid chelling of the melt, practically all
the P_2O_5 dissolves also in 2% citric acid.

Thus profound research and industrial experiences of long
standing in processing apatites and phosphorites by caking
and melting showed the advisability and effectiveness of
the production of defluorinated phosphates, suitable as
fertilizers in agriculture and as feed supplement in catt-
lebreeding. The product obtained is not only well assimi-
lative, but shows a great number of other technical and
economic advantages in comparison with products obtained
by acidic methods. They may be obtained without the expen-
diture of acid or with a small quantity of phosphoric acid.
They show a neutral or weakly alkaline reaction and are
practically non-hygroscopic. Their production can be was-
teless.

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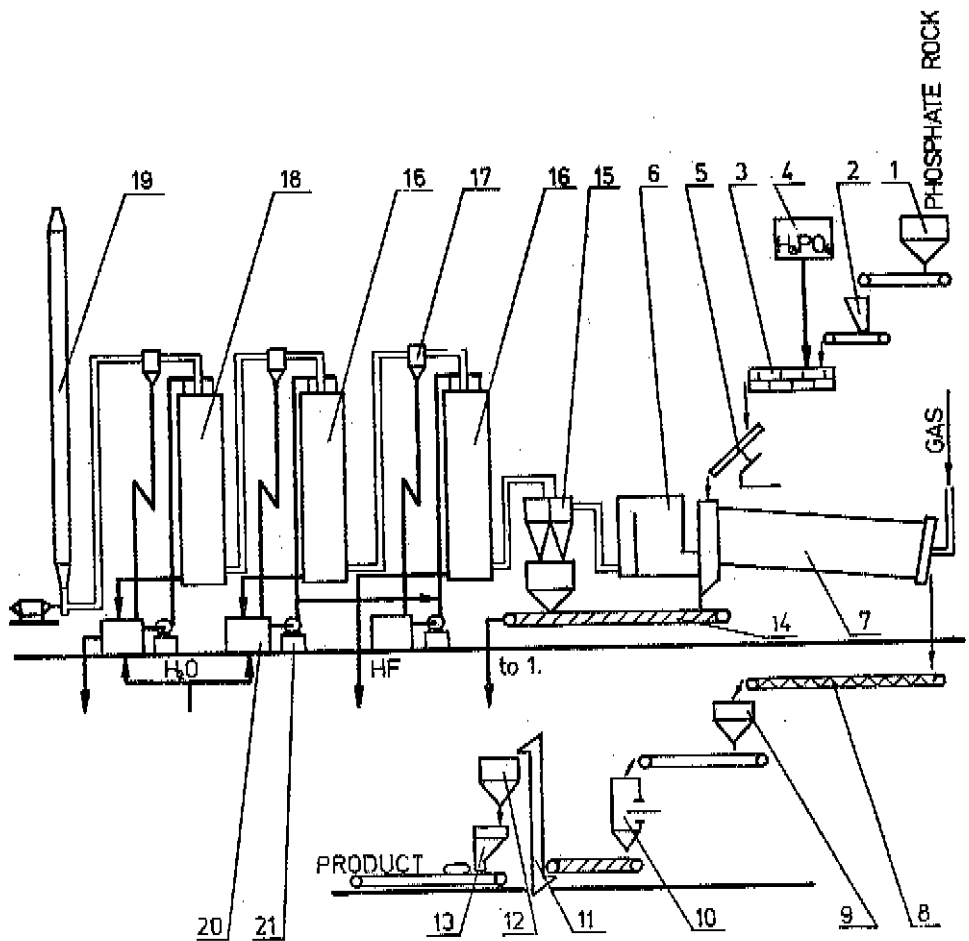
Fig. 1.   1 — phosphate bunker, 2 — dosator, 3 — double shaft
           mixer, 4 — phosphorus acid tank, 5 — disc granulator,
           6 — boiler, 7 — rotary furnace, 8 — clinker conveyor,
           9 — clinker bunker, 10 — desintegrator, 11 — elevator,
           12 — bunker of finished product, 13 — packing machine,
           14 — dust conveyor, 15 — battery cyclone, 16 — absorp-
           tion tower, 17 — spray trap, 18 — sanitary tower,
           19 — chimney, 20 — acid receiver, 21 — circulating
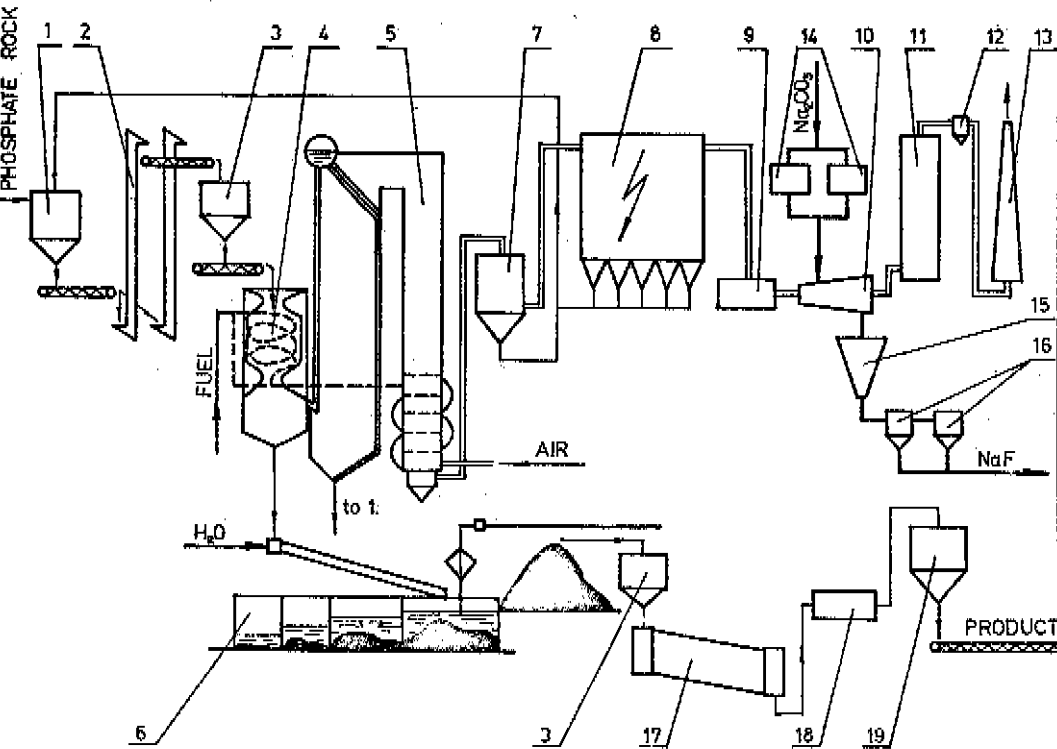   pump.

Fig. 2.   1 - phosphate bunker, 2 - elevator, 3 - bunker,
4 - cyclone furnace, 5 - boiler, 6 - basin,
7 - cyclone, 8 - electrical loader, 9 - collector,
10 - Venturi tube, 11 - absorption tower,
12 - spray trap, 13 - chimney, 14 - soda solution
tank, 15 - sedimentator, 16 - centrifuge,
17 - drying drum, 18 - ball mill, 19 - bunker of
finished product.