## Phosphoric fertilizers and phosphoric raw materials

The average phosphorus content in the earth's crust is less than 0.1% (or 0.25%  $P_2O_5$ ). The highest concentrations of  $P_2O_5$  are observed in igneous alkaline and basic rocks.

*Apatite Ca*<sub>5</sub>[PO4]<sub>3</sub>F(Cl, OH) is a compound with volcanic origin. Depending on the content, fluorine, chlorine, and hydroxylapatite are released.

Phosphorites are sedimentary rocks, a significant part of which are phosphates and numerous inclusions of other minerals (quartz, glauconite, calcite, clay minerals, etc.). The content of impurity elements is often observed: *U*, *Tr*, *Sr*, less often *V*, *Ti*, *Zr*, etc.:

- Simple superphosphate ( $Ca(H_2PO_4)_2 \cdot H_2O$ )- 19-21%  $P_2O_5$ .
- Double superphosphate  $(Ca(H_2PO_4)_2 \cdot H_2O) 42-50\% P_2O_5$ .
- *Phosphorite flour* ( $Ca_3(PO_4)_2 \cdot CaF_2$ )- 19-30%  $P_2O_5$ . Phosphorus in it is in a form inaccessible to plants and can be applicable only on acidic soils.
  - *Precipitate* (*CaHPO*<sub>4</sub>·2*H*<sub>2</sub>*O*)- 46-48% *P*<sub>2</sub>*O*<sub>5</sub>.

Methods for producing phosphate fertilizers:

- mechanical (grinding);
- thermal decomposition;
- chemical decomposition.

## Methods of production of double superphosphate:

- *Chamber method* using continuous superphosphate chambers and holding the product for ripening in the warehouse. For the decomposition of phosphates, thermal or extraction acid with a concentration of 50-58%  $P_2O_5$  is used.
- *Chamber-flow method* using similar chambers, but without the operation of warehouse maturation. To decompose phosphates, an extraction acid with a concentration of 47-49% is used.
  - Flow (tubeless) method using unpaired acid concentration of 30% P<sub>2</sub>O<sub>5</sub>.

Production of double superphosphate:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + 6.5H_2O = 3[Ca(H_2PO_4)2H_2O] + 7[CaSO_4 \cdot 0.5H_2O] + 2HF + 227.4 \text{ kJ};$$

$$Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O = 5[Ca(H_2PO_4)2\cdot H_2O] + HF.$$

Production of phosphoric acid by extraction

Sulfuric acid decomposition of calcium phosphate is a heterogeneous irreversible process occurring in the "solid-liquid" system and described by the equation:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + nH_3PO_4 + 5mH_2O = (n+3)H_3PO_4 + 5CaSO_4 \cdot mH_2O + HF.$$

Conditions for the extraction method for the production of phosphoric acid:

- the dihydrate method is carried out at 70-80° C, a concentration of  $P_2O_5$  in the liquid phase of 25-32%, a heat of reaction of 384.4 kJ/mol;
- the hemihydrate method is carried out at 95-100°C, the concentration of  $P_2O_5$  in the liquid phase is 38-48%, the heat of reaction is 371.0 kJ/mol.