

Yara's priority:

Fertilizers consists mainly of nitrogen, some of nitrogen and phosphorous, some of potassium and nitrogen and finally some of nitrogen, phosphorous and potassium. The basic raw materials used in the Yara Odda fertilizer process are phosphate rock for phosphorous, nitrogen from the air and potassium chloride/sulphate. The main sources for phosphate are the minerals apatite and phosphorite. Yara buys these phosphates from different companies in the world, in addition Yara owns the Silinjervi phosphate mine in Finland.

The phosphate rock contains a lot more elements than just the phosphate. Actually, the whole periodic table is present in different concentrations, depending on the origin of the material. Two typical phosphate rocks exists, the phosphorites (francolite) , a sedimentary type of material and the apatites , an igneous type of material. The world phosphate reserves estimated today, consists of 80-85% sedimentary rock. The by far largest reserves are found in Morocco. Morocco is also the world's largest phosphate producer. Actually all the north African countries have sedimentary phosphate reserves in different quantities and qualities, from Morocco on the west coast to Jordan. Phosphates are very a common mineral found in many places in the world.

The characteristics of the two different types of phosphate rocks are showed below:

Apatites: $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	Francolite: $\text{Ca}_{10}(\text{NaMg})(\text{PO}_4)_6((\text{CO}_3)(\text{CO}_3\text{F})(\text{SO}_4))\text{F}_2$
P, % : 16-17,5	P, % : 10-14
Ca/P : 2,2-2,3	Ca/P : 2,3 ++
F, % : 2,4-3,2	F, % : 3,5-3,9
CO_2 , % : 0,1-0,5	CO_2 , %: 1-5
Heavy metals / radioactivity : Low	Heavy metals / radioactivity : High
Cd: < 10 mg/kg P	Cd > 50 – 500 mg/kg P
Organic material: <0,1 %	Organic material: 0,1 – 5 %
Rare earths > 0,25-1,3%	Rare earths <0,2 %

Yara has a phosphate rock specification, describing the chemical composition of the material that can be used in the plant.

This specification contains certain elements with concentration limitations. These limitations are based on operational issues and legislation. Examples in this context is chloride which makes a very corrosive mixture with nitric acid. Another example is cadmium where certain countries have limits on the level in fertilizers. There are also certain high value elements that can be extracted from the process.

At the moment and for some years Yara has been / is complying with their rock specification by mixing rocks bought on the commercial market. For the future it is believed that more sedimentary material will be the main source for fertilizer phosphorous. As can be seen from the general description of apatites and francolites, the sedimentary rocks carries heavy metals, organic material and also radioactive elements to a higher level than apatites. The different phosphate rocks contains different elements. As Yaras goal is to be a "green" fertilizer producer, it will have to process the sedimentary material, while at the same time, for some of the phosphates, remove some of the unwanted elements in the production process. This is a situation Yara wants to prepare for.

Yaras Odda fertilizer process is based on digesting of phosphate rock in 65 % nitric acid. After removal of undigested material the solution is cooled down to 0 °C to crystallize $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. In this way 75% of the calcium present in the phosphate rock is removed. The calcium nitrate is filtered from the solution and sold as a fertilizer. The solution is further neutralized with ammonia, evaporated, mixed with a potassium salt and prilled. The final NPK product is coated, packed and sold.

The removal of the unwanted elements and the recovery of the valuable elements would preferably have to take place in the acidic part of the process as the elements are still in the ionic state. Some neutralization is possible before calcium and the rest of the cations starts to precipitate. As the phosphate rock contains basically the whole periodic table of elements in different concentrations, it becomes a challenge to selectively remove some of them. According to Van Kauwenbergh: "Cadmium and other minor elements in the world resources of phosphate rock", The fertilizer society, London oct. 1997, the elements expected to be focused for potential future removal are the following. As, Cd, Cr, Hg, Pb, Se, U and V. As mentioned earlier, the phosphate rocks are different and carry these elements in different concentrations. For some rocks arsenic could be a problem, for others cadmium.

It is known that some of the phosphate rocks contains valuable elements, like rare earths. All though in small quantities, < 1,3 %, the big throughput in a fertilizer plant, still makes it an interesting volume. Yara did produce rare earths in the late 90-ties in their plant at Glomfjord. The process was based on Kola phosphate rock. It is presented in: Al-Shawi, A, Engdal, S.E., Jensen, O.B., Jørgensen, T.R., Røsæg, M.: "The integrated recovery of rare earths from apatite in the Odda process of fertilizer production by solvent extraction. A plant experience." ISEC conference, Johannesburg, South Africa 2002.

The challenge is, for the removal of the unwanted elements and recovery of valuable elements to make a safe, cheap, robust and simple process. On order to achieve this the fundamental chemistry must be known and utilized in an industrial way.

Yara has over the last years increased their effort in R&D and innovation. We have recently built a multipurpose pilot plant at the research centre in Porsgrunn. This plant fits well to the hydrometallurgical experiments that would have to be carried out to develop processes for the issues presented.