THERMAL PHOSPHORUS – IT'S A HOT COMMODITY WITH A HOT PROCESS

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ABSTRACT

Yellow phosphorus (YP) has been commercially produced since the 1920's. First in the USA by the Tennessee Valley Authority (TVA), next in Russian (Kazakhstan) in the 1950's and finally in China in the late 1970's early 1980's. There are operations in Vietnam and Sarawak on a smaller scale.

YP has become very in vogue due to its use in the production of lithium iron phosphate battery cathode precursor materials by the Chinese and other western battery manufacturers. The YP is also used to produce purified phosphoric acid and higher grades of acid using a thermal oxidation process after smelting.

This paper will look at the basics of the smelting including slag chemistry, alloy chemistry and off gas chemistry. The paper will look at the design of the furnaces used in the YP production process as well as the downstream recovery of phosphorus from the smelter off gas stream to YP.

The next part of the discussion will focus on the operations of a YP smelter with regards to control of the furnace to optimise phosphorus recovery to YP. Will discuss tapping cycles for alloy and slag with a view to optimal phosphorus recovery.

The discussion will close out with a review of operational challenges in the smelter and a brief description of the downstream conversion of YP to high purity phosphoric acid.

INTRODUCTION

The production of phosphorus via the thermal route has seen a resurrection in popularity in the last few years due to the need for increased amounts of purified phosphoric acid (PPA) for use in lithium ion battery (LIBs) cathode assemblies utilising lithium iron phosphate (LFP). Operators do not need to rely on large wet process phosphoric acid production facilities for the production of purified phosphoric acid (PPA).

The technology employed today has remained unchanged for more than 80 years. The original thermal phosphorus production was conducted in small blast furnaces in the USA in the Tennessee Valley authority (TVA). Later in the late 1940's the production of thermal phosphorus began to appear in Russia in Kazakhstan (Karatau region). A series of phosphorus chemical facilities were developed around the low grade sedimentary phosphate ores of the region. These same facilities are still in operation today. In the late 1970's and early 1980's the Russian based technology was seen to be developing in China in the eastern part of Yunnan Province. The metallurgical process for the production of thermal phosphorus relies on the use of hard lumpy ore combined with metallurgical coke (reductant) and silica (flux). It is worth noting that thermal phosphorus production facilities have been constructed in Vietnam and Sarawak where power costs (hydroelectric) are lower than countries using fossil fuel generated power.

The predominant furnace design is a closed top electric submerged arc furnace with twin slag tap holes and a single alloy tap hole located between the two slag tap holes.

METALLURICAL BASICS OF THERMAL PHOSPHORUS PRODUCTION

The production of thermal phosphorus relies on thermal energy to liberate elemental phosphorus from its oxide form and subsequently produce phosphoric acid. This carbothermal reduction process is typically conducted within two major process units: the Yellow Phosphorus (YP) plant and the downstream Thermal Phosphoric Acid (TPA) plant.

The reaction, which is endothermic, between phosphate rock, silica, and coke (carbon source) is as shown in equation 1 below at a reaction temperature greater than 1,100°C. Optimum reaction temperature is between 1,400°C-1,600°C. Temperatures over 1,700°C will not only result in unwanted side-reactions but also increases energy consumption.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 10CO + 6CaSiO_3 \qquad \textit{Eq1}$$

Typical material characteristics

The production of YP requires phosphate ore, carbon reductant and silica. Table 1, Table 2 and Table 3 below illustrate some typical chemical analyses for the materials concerned.

Table 1 - Phosphate ore specification

Species	**P_2O_5 (%)**	**S (%)**	**SO_3 (%)**	**MgO (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**As (ppm)**	**Na_2O (%)**
Target	>= 28.0	N/A	<+1.75	<=0.35	<=0.65	<=1.90	<=20	<=0.45
Species	**K_2O (%)**	**Cl (%)**	**F (ppm)**	**LOI (%)**	**CaO (%)**	**SiO_2 (%)**	**H2O (%)**	**Pb (ppm)**
Target	<=0.06	<=0.06	<=27500	<=6.25	<=46.5	>+10.0	<=4.0	N/A

Table 2 - Carbon Reductant Specification (Metallurgical Coke)

Analysis item	**Specification**	**Unit**
Fixed Carbon	≥ 80.0	% w/w
Volatile Matter	≤ 1.5	% w/w
Ash	≤ 18.0	% w/w
Total Sulphur	≤ 1.0	% w/w
Moisture	≤ 5.0	% w/w
Particle size range	10-25	mm

Table 3 – Silica Specification

Analysis item	**Specification**	**Unit**
SiO_2	≥ 95.0	% w/w
CaO	≤ 0.01	% w/w
Al_2O_3	≤ 0.2	% w/w
Fe_2O_3	≤ 0.5	% w/w
MgO	≤ 0.008	% w/w
Particle size range	20-50	mm

Thermodynamics of yellow phosphorus smelting

As stated in the introduction, this process is a carbothermal reduction process whereby phosphate ore (P_2O_5) is combined with a carbon reductant (metallurgical coke) and a flux (silica). The process reaction is illustrated in equation 1.

Fluxing strategies for phosphate ore are based on the need to achieve fluid slags with a low liquidus temperature.

Potential operating temperatures have been observed between 1,340°C and 1,450°C, depending upon the ore chemistry and quantity of flux addition. Recovery of phosphorus to the furnace off gas stream has been observed to decline as slag volumes increased, or if the Fe content in the ore increases above approximately 2.3%.

The furnace conditions were noted by Kennedy (2017), as being highly reducing which is required to fume the phosphorus as P_2, and the CO/CO_2 ratio in the off gas can be between 105 and 107, depending upon the temperature, chemistry and final phosphorus content of the slag.

Slag Chemistry

It has been said that if you take care of your slag it will take care of you (and your process). YP smelting is no different. The slag chemistry of the phosphate smelting process relies on the carbothermal reduction of P_2O_5 to P. In ferro alloy smelting one is always watch the viscosity of the slag so as to minimise product losses to the slag.

In YP production the P losses are caused when the ore has >2.3% Fe in the ore which readily complexes with the P to form an iron rich phosphorus (FeP) alloy.

As can be seen in Table 1, the ore specifications call for a low Fe, MgO and Al_2O_3 contents.

The key base slag systems are the Al_2O_3-CaO-SiO_2 system as shown in Figure 1 and the CaO – SiO_2 – P_2O_5 system Figure 2. The Al_2O_3-CaO-SiO_2 system has previously been extensively studied by Maun et al.

A typical slag analysis for YP smelter slag is shown in below in Table 4.

Table 4 – Typical YP Smelter slag analysis

	P as P2O5 (%)	Al as Al2O3 (%)	Mg as MgO (%)	Fe as Fe2O3 (%)	Sulphur, S (%)	Ca as CaO (%)	SiO2 (%)	Mk Ratio (SiO2 + Al2O3) / (CaO + MgO)	Basicity (CaO + MgO)/ SiO2
Control Range	1.0 - 3.0	2.0 - 5.0				40.0 - 50.0	35.0-42.0		
Values	0.87	3.52	2.77	0.34	0.95	48.81	38.75	0.82	1.34

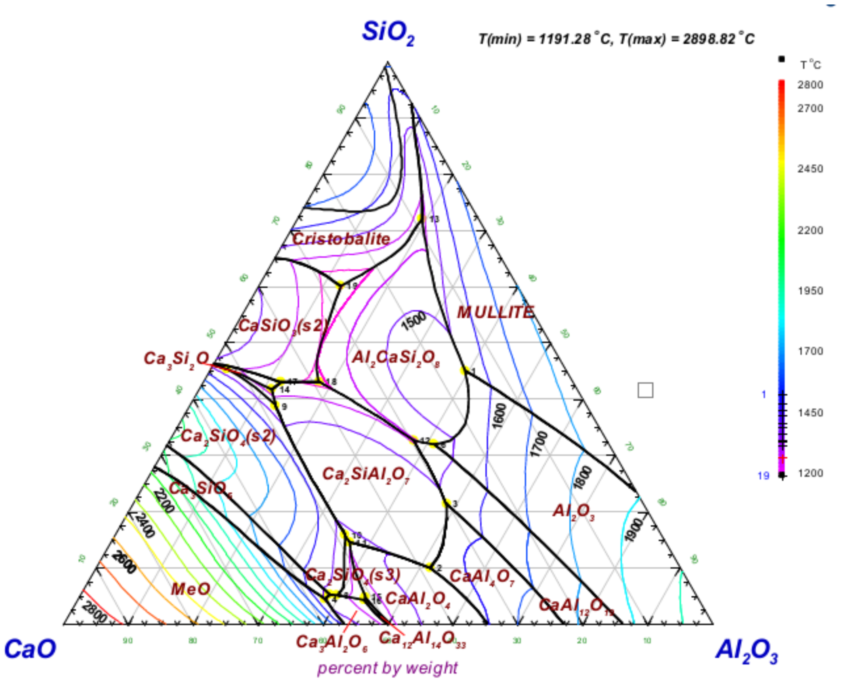

Figure 1: Al_2O_3 – CaO – SiO_2 phase diagram (weight %)

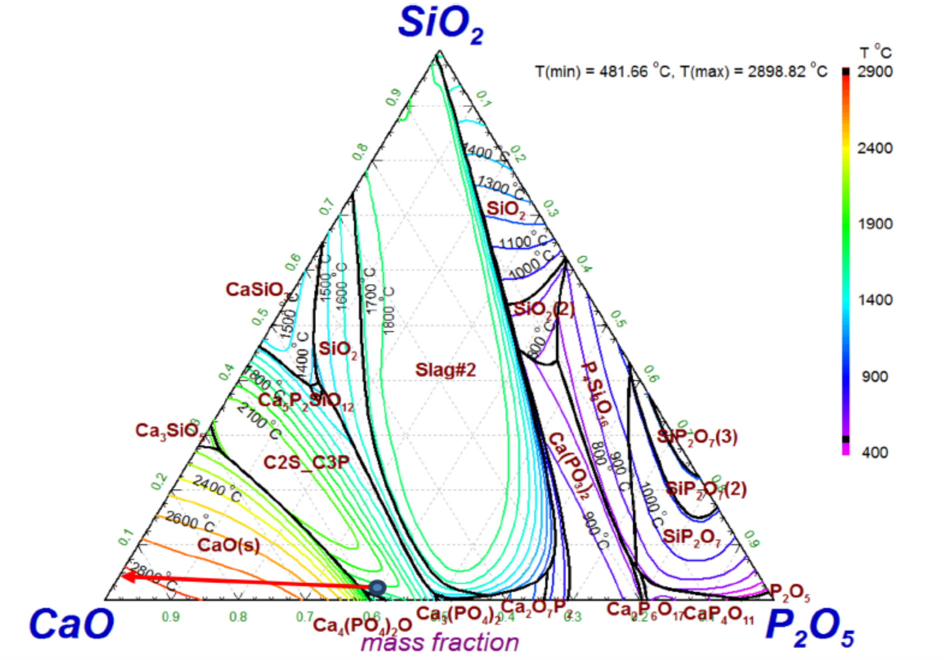

Figure 2: CaO – SiO_2 – P_2O_5 phase diagram (weight %),

The Russian thermal phosphorus production industry derived a dimensionless metric to measure the basicity of the slag called the Mk value which is the ratio of acidic oxides (SiO_2 + Al2O_3) to basic oxides (CaO + MgO) in the slag. The Chinese YP operations have adopted the same metric to assess their slag chemistry. In ferro alloy smelting use is made of the basicity ratio which is the ratio of basic oxides (CaO + MgO) versus acidic oxides (SiO_2). Noting that the basicity ratio treats Al_2O_3 as amphoteric and therefore is left out of the calculation.

Phosphorus fuming

The recovery of phosphorus from the ore to gaseous phosphorus is driven by the ability to remove the P gas from the furnace burden as quickly as the burden porosity allows.

The typical industrial furnace smelting operating temperatures are recorded as being between 1,450°C and 1,340°C, depending upon the ore chemistry and quantity of flux addition. Recoveries are reduced as slag volume increased or if the Fe content in the ore/concentrate increased.

The highest phosphorus recoveries to the fume were for ores which have low iron contents. As iron and phosphorus “like each other”, phosphorus will alloy with iron in the solid state as well as the liquid state, recovery will be affected by the iron content of the feed.

PROCESS PLANT OPERATION

Figure 3 illustrates the process flow for the production of YP via the smelting route. Phosphate rock (lump), silica and metallurgical coke is delivered to the YP plant where materials are unloaded and conveyed to their respective covered storage sheds. The phosphate rock, silica and metallurgical coke are recovered by front end loaders and conveyed via their respective sizing and screening circuits to the raw materials proportioning area storage bins. The sized raw materials are then batched according to a preset material recipe which caters for the amount of carbon required per tonne of phosphate ore, is conveyed and stored in dedicated furnace day storage bins.

The proportioned feed is fed via vertical chutes into the furnace. The material feed proportions are primarily based on P_2O_5 to fixed carbon ratio as well as silica to calcium oxide ratio. However, contents of other species (e.g., sulphur and iron) should also be considered, which could affect silica and carbon (coke) feed rate relative to phosphate rock.

The furnace most commonly used is a closed top submerged electric arc furnace. The furnace is equipped with cylindrical, pre-baked graphite electrodes that are vertically hung via suspension cables or water-cooled electrode hoists and clamps.

Typical energy consumption data shows the average power consumption to be approximately 13 to 15 MW per tonne of YP. The furnace produces molten slag and ferro phosphorus alloy as by-products. The slag (calcium silicate) is typically tapped every four hours into a launder and directed into a water granulation system. The ferro phosphorus alloy is tapped every eight hours into small sand moulds where the ingots are allowed to cool before being removed to a storage area. The furnace off gas stream, which is rich in phosphorus, carbon monoxide, hydrogen and fine particulates exits the furnace via an off-gas duct to the gas scrubbing and phosphorus recovery circuit. The phosphorus rich off gas is passed through an electrostatic precipitator where the fine particulates are removed ahead of the multistage phosphorus recovery condensers. The phosphorus gas in the condensers is condensed to liquid phase by water sprays.

The liquid phosphorus and the spray water from the condensers flows by gravity into a collection sump. Although most of the dust and particulates in the off-gas stream will have been captured by the electrostatic precipitators, some carryover of these contaminants can be expected in the condenser outlet stream. In the collection sump, the liquid phosphorus, which is denser than the water will separate out and settle at the bottom. The particulates, however, will be distributed between the water and phosphorus layers.

The water (plus fine particulates) is separated from the yellow phosphorus and transferred to holding tanks (settlers) to separate out the solids (sludge or mud) from the water. The water will then be recycled to the spray condensers. Neutralization may be required depending on the pH of the water stream. The liquid YP is next pumped to purification tanks to separate out the remaining solids. The clean YP will be pumped to storage, while the sludge will be transferred to sludge (mud phosphorus) tanks. Low Pressure (LP) steam will be supplied to the tanks and piping system to maintain the temperature of the YP at ~80°C. Noting that YP solidifies at 45°C.

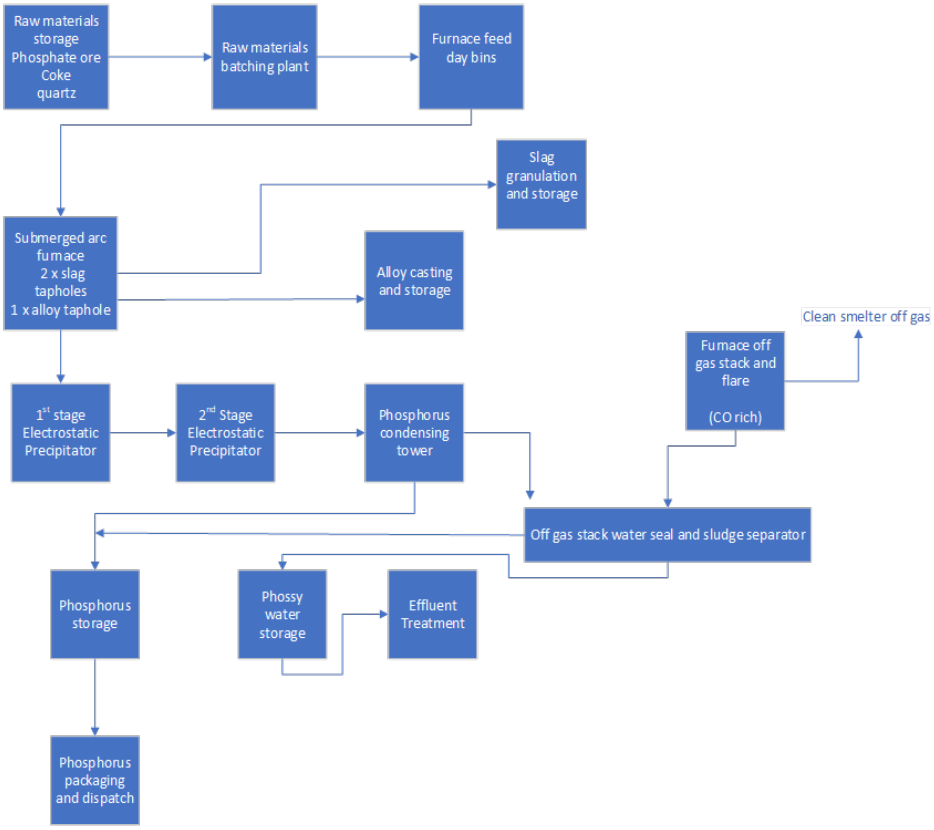

Figure 3: Diagram of yellow phosphorus smelting system.

The clean YP is then pumped from the YP storage tanks to the downstream thermal phosphoric acid facility where technical grade phosphoric acid is produced.

PROCESS CHALLENGES

The production of YP from phosphate ores comes with its own set of challenges. These range from energy efficiency of the smelting process through contaminant management in the YP to ore and reductant quality and sources.

Ore

The traditional production of YP has relied on the availability and use of lump ore (25mm to 75mm) in electric submerged arc furnace smelting operations. As the availability of lump ore dwindles, and the cost of lump ore increases, there is a need to look at the use of phosphate concentrates (fines) that have been agglomerated into similar sized briquettes as the lump ore. The briquetting of ore is simple and one of the better binders is phosphoric acid which acts with the calcium in the ore to produce hard mechanically robust lumps. The challenge lies in the fact that with China currently the leader in YP production they also have certain set ideas about ore substitution in the YP furnaces. Chinese YP production limits the mass of briquettes to a maximum of 30% by total ore mass per batch. The reason given is that the furnace operation becomes unstable above 30%.

It is worth remembering that in ferro chrome (FeCr) production in the years prior to the late 1980's, use was made of lump chromite ore in deep hearth submerged arc furnaces. As the lump chromite ore supplied dwindled, it became necessary to develop ways of using the chromite fine concentrates that were readily available. The result was the development of chrome ore pelletising followed by sintering to produce feed for the FeCr furnaces. Allied to the smelting of chromite pellets was the redesign of the furnace hearths to have a shallower hearth so as to allow the gases to exit the furnace.

This line of thinking needs to be tested and applied to the production of YP so as to be able to access cheaper phosphate ore supplies.

Carbon Reductants

Metallurgical coke has been used as the reductant of choice for many years due to its availability and cost. Today there is a move towards using reductants that are manufactured from biomass thus creating bio chars and bio coke products. One of the key attributes for the reductant in the YP smelting process is to have good mechanical strength so as to maintain the furnace burden porosity so that the P rich off gas can easily exit the furnace.

Waste Heat Recovery

The smelting process produces a final scrubbed off gas with a CO rich off gas. Table 5 illustrates a typical off gas chemistry as reported by Feng (2017). The energy from the off gas can be used to raise steam for local district heating. In operations where briquetting is carried out, the waste heat can be used to dry the green briquettes. Alternatively, the steam can be used for local cogeneration of electrical power.

Table 5 – Typical YP Smelter off gas analysis

Species	CO (%)	CO_2 (%)	O_2 (%)	H_2 (%)	CH_4 (%)	N_2 (%)	H_2O (%)	H_2S (mg/m^3)	PH_3 (mg/m^3)
Range	87	1	0	1	0	2	0	800	500
	92	4	1	8	0.3	5	5	1100	1000

YP Process Slag Valorisation

The smelting of phosphate ore produces approximately 7 to 9 tonnes of slag per tonne of YP during the smelting operations. The slag is usually granulated in water baths. The resultant product is a gravel like slag that is dumped on stockpiles to dewater. The slag is predominantly a calcium silicate slag which can be used as feedstock into cement manufacturing as a cement extender similar to the addition of fly ash to cement grinding.

Other uses of the slag are as aggregate replacement in cinder block manufacturing and in gravel replacement materials.

Alternative Smelting Technology For Phosphate Smelting

Research is being considered to investigate the use of DC arc furnace technology for open bath smelting of phosphate ore. Given the main product is a fumed phosphorus gas in the furnace off gas. The rationale draws on the experiences gained in South Africa at Mintek where open bath DC arc furnace smelting of zinc oxides was piloted to assess the fuming of zinc.

The potential to make use of open bath DC arc smelting for YP production means operators could possibly make use of phosphate fines directly with finer carbon reductant products. This would be a game changer in the YP production space as this would potentially reduce the cost of production due to cheaper ore prices.

Carbon Footprint

The production of YP is highly energy intensive. It is therefore essential to conduct a preliminary estimation of the greenhouse gas (GHG) inventory or carbon footprint for the conversion of mined phosphate rock to YP and identify potential reductions and elimination where possible. The following should be considered in the design phase:

- Incorporate emissions impact into decision making on logistics, facility location and process design.
- Carbon emission costs and tax calculations.
- Identify opportunities to potentially reduce the carbon footprint, which could also potentially improve the efficiency of the process. This may include alternatives to metallurgical coke as carbon reductant, waste heat recovery, electrification by way of renewables for operations where possible, and gas scrubbing to remove CO_2 and inclusion of CCS technologies.
- Identify potential cost-saving opportunities.
- Demonstrate environmental and corporate responsibility to potential investors and off-takers.

CONCLUDING REMARKS

The smelting technology employed in the production of YP has remained the same for nearly 80 years. The use of submerged arc furnaces appears to offer the best process control for the fuming of the P from the ore.

The next stage in the evolution of the process will be the development of furnaces that can make use of concentrates rather than lumpy ore. This may lead to the potential use of DC arc furnaces for the fuming of P. Another area of development will be the adoption of bio coke in place of the traditional metallurgical coke manufactured from coking coal.

That said the YP process route for the production of purified phosphoric acid (PPA) for use in battery cathode assemblies will remain popular due to its lower capex than that associated with the traditional wet phosphoric acid production process.

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