

PHOSPHATE: OXO CUBES, MARMITE, AND MATCHES



This is the first in a series of articles on phosphate and phosphate mining and is intended as being an amuse-gueule before we start on the technical stuff.

In the 19th Century, Justus von Liebig developed the first mineral-based fertilizers, overturning the popular belief that organic material was required for plants to grow. Liebig is generally credited with formulating the “Law of the Minimum” (1840), which states that the efficacy of plant growth will be determined by the element which is least abundant, even if all other elements are present in great abundance. It is worthwhile noting that Carl Sprengel (1787–1859) had already published similar research, however, he was not credited with the discovery. Justus von Liebig was one of the first to attempt the development of a mineral-based fertilizer by treating phosphate of lime derived from bone meal with sulfuric acid.

So why phosphate? To answer that question, we need to consider how soil can sustain and yield crops of high quality. In order to do so, soils need to be rich in both macro and micronutrients; arguably the most important of which are potassium, nitrogen, and phosphorus (the NPK Ratio that you see on bags of fertilizer, often referred to as the macro-nutrient trinity).

Of the three macro-nutrients, only nitrogen can be manufactured using the Haber–Bosch (HB) process, developed in Germany during World War One for military purposes. Ammonium nitrate (AN) is predominantly used as a high-nitrogen fertilizer but is also the major constituent of ANFO (ammonium nitrate/fuel oil), which is why fertilizer is the “go to” raw material for domestic terrorists. AN is also used as an oxidizer in rocket fuel and to help deploy airbags in cars.

Prior to the development of the HB process, nitrate was only available in caliche deposits in its natural form, nitratine. Limited supply of this material (primarily for the use in explosives),

resulted in the War of the Pacific (1879 to 1884) that took place between Chile and a Bolivian–Peruvian alliance. Nitratine is used in organic farming where HB nitrates are forbidden.

Phosphorus, the second of the macro-nutrient trinity, is always found in the oxidized state due to its highly reactive nature. It is essential to life, occurring in DNA, RNA, and the ADP/ATP energy cycle. It was the first modern element to be discovered (1669, Hennig Brand) using the scientific method. Brand was searching for the Philosopher’s Stone, or gold – stories vary (Brand was an Alchemist like Nicolas Flamel of Harry Potter fame). Brand had decided to experiment with urine. During his endeavours, Brand extracted a white mineral that glowed in the dark and burnt brilliantly, this he named “phosphorus mirabilis” (latin for “miraculous bearer of light”).

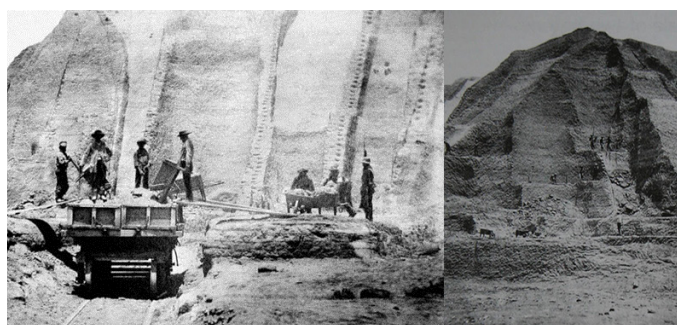
Early phosphorus production was initially derived from burning bones to create bone ash (1840s). In 1802, Alexander von Humboldt (an Austrian explorer) encountered guano in Peru and started to investigate its fertilizing properties, having no doubt learned of its use from the Quechua people (the Inca being the best-known). In 1813, Humphry Davy (of safety-lamp fame) published a book extolling the virtues of guano as a fertilizer, this in turn led to a demand for the product and two wars:



- Chincha Islands War (1864 to 1866): fought between Spain and its former colonies of Peru and Chile.
- War of the Pacific (1879 to 1884): fought between Chile and Bolivia.

America too, got in on the act, passing the Guano Islands Act in 1856. This act, which has never been repealed, "enables citizens of the United States to take possession, in the name of the United States, of unclaimed islands containing guano deposits. The islands can be located anywhere, so long as they are not occupied and not within the jurisdiction of another government. It also empowers the President of the United States to use the military to protect such interests and establishes the criminal jurisdiction of the United States in these territories".

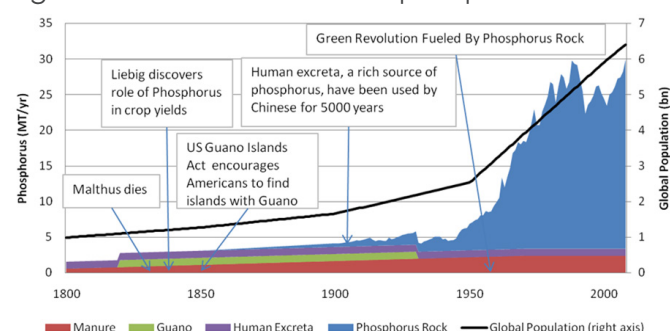
Figure 1. Examples of guano mining



Source: <https://99percentinvisible.org/episode/guano-mania/>

As organic phosphate supplies ran out, alternative sources had to be found, and this is where our story proper commences. The first documented phosphate rock mining commenced in England in 1841. Large, high-quality, near-surface, sedimentary deposits were being discovered in Florida (USA) in the 1880s by Captain J. Francis LeBaron, of the United States Army Corps of Engineers (Figure 2), allowing America to dominate the phosphate market for decades to come.

Figure 2. Historical sources of phosphate



Source: https://staticseekingalpha.a.ssl.fastly.net/uploads/2010/1/13/345817-126341342065185-engstudent_origin.png

Most phosphate deposits are associated with sedimentary rocks of marine origin (87%), with the remainder being derived from igneous (Phanerozoic carbonatites and silica-deficient alkalic intrusions) sources (Note: the numbers may vary depending on the source consulted). Sedimentary phosphate deposits generally contain >18 wt % P₂O₅, while igneous deposits contain between 5 to 15 wt% P₂O₅.

Other elements are also present in sedimentary and igneous phosphate deposits, including uranium (U) and rare earth elements (REEs); with the concentration of U being as high as 3,000 ppm in sedimentary deposits. Other heavy metals might also be present, including arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), and vanadium (V). The presence, or rather absence, of Cd in a phosphate deposit might be a deal breaker, as it is classified as a class-one carcinogen by the World Health Organization (WHO). However, high levels of Cd can be reduced via blending. An example of this was where high-grade phosphate from Togo (a sedimentary deposit associated with high Cd levels) was blended with ore from South Africa's Phalaborwa deposit (a carbonatite deposit, containing 0% Cd).

So, what makes a "good" phosphate ore (in terms of quality)? Some quality guidelines are suggested in Table 1.

Table 1. What makes a "good" phosphate deposit

Impurity	Practical levels for Phosacid production	Target levels
P ₂ O ₅	28-40% P ₂ O ₅	32% P ₂ O ₅
Al ₂ O ₃	0.2 - 2.0% Al ₂ O ₃	Fe ₂ O ₃ + Al ₂ O ₃ < 2-3%
FeO	0.1 - 2.0% Fe ₂ O ₃	Fe ₂ O ₃ + Al ₂ O ₃ < 2-3%
MgO	0.2 - 2.0% MgO	<1.5% preferred, <1% ideal
MER ratio	0.05 - 0.12 (Al ₂ O ₃ + Fe ₂ O ₃ + MgO) / P ₂ O ₅	<0.1 preferred
CaO/P ₂ O ₅ ratio	1.30-1.65 CaO/P ₂ O ₅	1.32-1.55:1 preferred, <1.6:1 generally accepted
Fluorine	2-4% F	<4%
Silica	1-10% SiO ₂	<5% preferred
Chlorine	0.00 - 0.05% Cl	<300ppm, preferred, <500ppm acceptable
Organics	0.1 - 1.5% C	<1% preferred, <0.2% ideal
Cadmium	up to 250ppm	<5ppm is premium, <2ppm meets strictest standards

Note the presence of silica as a contaminant... the use of quartz blanks may not be such a good idea when running an independent QA/QC programme...

1. OXO cubes, Marmite, and Matches

So how do we tie phosphate to OXO cubes, Marmite, and matches? The first bit is relatively easy, once again Justus von Liebig is involved. Amongst his many other discoveries, he developed a manufacturing process for beef extract, and with his consent, a company called Liebig Extract of Meat Company, was founded to exploit the concept; it later introduced the OXO cube.

Marmite, that English breakfast staple and preventer of beriberi due to its high vitamin B1 content, was invented when von Liebig discovered that brewer's yeast could be concentrated, bottled, and eaten. The Marmite Food Extract Company was founded in England in 1902, with the by-product yeast required supplied by Bass Brewery, manufacturers of Bass Pale Ale, once the highest-selling beer in Britain.

And matches you may ask? Matches of the type known to Hans Christian Andersen's "The Little Match Girl" were referred to as "lucifers"; the tip of which contained white phosphorus (WP), a highly toxic material. Ongoing exposure to phosphorus fumes resulted in the destruction of the jawbone, hence the term Phossy Jaw.

Figure 3. Phossy Jaw



Source: https://en.wikipedia.org/wiki/Phossy_jaw#/media/File:Match_factory_worker_with_phossy_jaw.jpg

Following the Matchgirls' strike of 1888, red phosphorus, a much less toxic material, replaced WP. In 1906, the Berne Convention (formally the International Convention respecting the Prohibition of the Use of White/Yellow Phosphorus in the Manufacture of Matches) outlawed the use of WP in matches. However, it remains in use by the military where it is referred to as "Willie Pete".

So next time you watch Peter Jackson's "They Shall not Grow Old", the lyrics of this song might make a little more sense:

"Pack up your troubles in your old kit-bag
And smile, smile, smile,
While you've a lucifer to light your fag,
Smile, boys, that's the style.
What's the use of worrying?
It never was worth while
So pack up your troubles in your old kit-bag
And smile, smile, smile."

Next time: Marion King Hubbert and the Peak phosphorus scare

Further reading

Brown, G.I., (1998); The Big Bang: A History of Explosives.

Emsley, J., (2001); The Shocking History of Phosphorus: A Biography of the Devil's Element.

Pufahl, P.K, (2017), Sedimentary and Igneous Phosphate Deposits: Formation and Exploration: An Invited Paper, Economic Geology, 112, pp 483-516.

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