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Phosphate Fertilizer Production – From the 1830's to 2011 and Beyond

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1. Early fertilizer production

In 1835 Gotthold Escher pointed out the value of bone as a fertilizer and suggested a “cheap and not too strong acid” to decompose the bones before applying to the soil. Later in 1840, the Duke of Richmond stated that the fertilizer value of bones was due to the phosphoric acid that they contained. In that same year, Justus Von Leibig added sulfuric acid to crushed bones to make them more soluble and proved that phosphate of lime and not gelatin was the fertilizing agent in the material. In 1843 he proved that phosphate of lime performed identically whether obtained from bones or phosphate rock.

John Bennet Lawes, founder of the Rothamstead Experiment Station in Harpenden, England, put Leibig's suggestions to practical use and began to manufacture artificial fertilizer in Deptford, London (See Figure 1), by mixing sulfuric acid with crushed bones and coprolites. He called his product “superphosphate”. Although Lawes has been credited with the first commercial success in the manufacture of superphosphate, he was not, contrary to popular belief, the inventor of the substance. The first commercial production of superphosphate was actually carried out by Sir James Murray. In his pamphlet “Advice to Farmers”, Murray described a formulated mixture consisting primarily of superphosphate produced by treating crushed bones with sulfuric acid.

English patents for the manufacture of superphosphate were granted to both Murray and Lawes on the same day, May 23, 1842. Murray, however, had received a Scottish patent several weeks prior to this date. Ten years after the patents were granted, Lawes purchased Murray's patent. By 1845, the bone crushing factories of England were being converted into superphosphate factories and the commercial phosphate fertilizer industry was launched.

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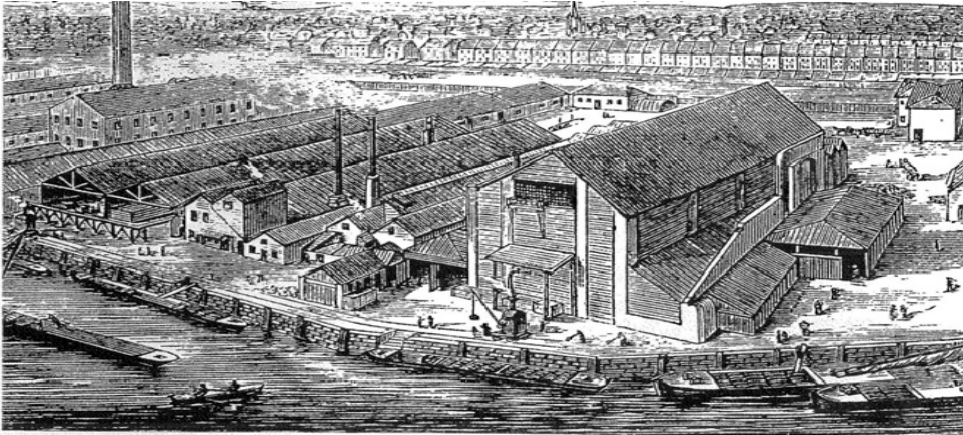


Figure 1: The first factory for the manufacture of superphosphate fertilizer at Deptford Creek, 1843

2. The rise of Di ammonium phosphate

Higher analysis fertilizers incorporating both nitrogen and phosphorous were the next step in the development of the fertilizer industry. Mono-Ammonium Phosphate (MAP) production began in about 1920. Major Di-Ammonium Phosphate (DAP) production began in about 1954. DAP is now, of course, the most widely traded phosphate fertilizer in the world with about 31 million tonnes being produced in 2009.

In the original Dorr-Oliver process, the ammoniation was carried out entirely in reaction vessels. Three reactors were used in series operating at 0.6, 1.4 and 1.85 mole ratio respectively. The slurry from the final reactor flowed by launder to one or more pugmills or blungers (See Figure 2). Because of the relatively insoluble nature of the slurry at 1.85 mole ratio, large amounts of water (30% or higher) were necessary to enable the slurry to flow. As a consequence these early plants operated with a large recycle ratio of up to 12/1. Some refinements were made to the process whereby partial ammoniation was carried out in two vessels and the remaining ammonia added in the pugmill. This technique enabled recycle ratio to be reduced to about 8/1.

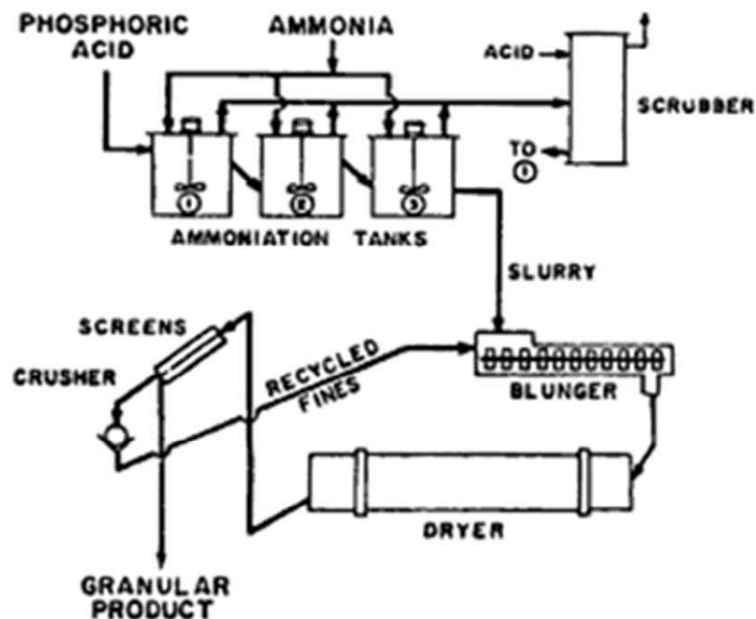


Figure 2 : Original Dorr-Oliver process.

A major break-through came in 1956 when Frank Nielsson of TVA patented the Ammoniator-Granulator (See Figure 3). This invention allowed large quantities of ammonia to be injected beneath the rolling bed of wet solids in a rotary drum with reasonable efficiency. In the TVA process only one “preneutralizer” vessel was used, operating at the point of maximum solubility (mole ratio 1.4-1.45) to minimize the slurry moisture (16-20%). This enabled recycle ratio to be reduced to about 5/1. Modern plants have demonstrated that, with some tweaking of process conditions, this basic process can be operated at a recycle ratio of about 4/1.

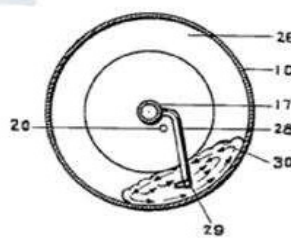
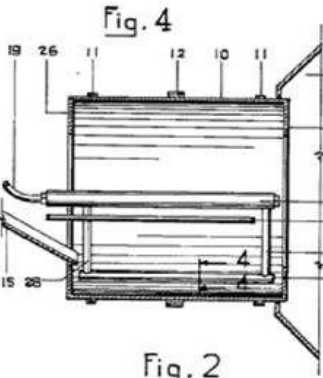
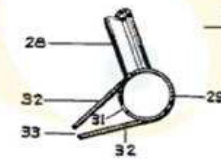
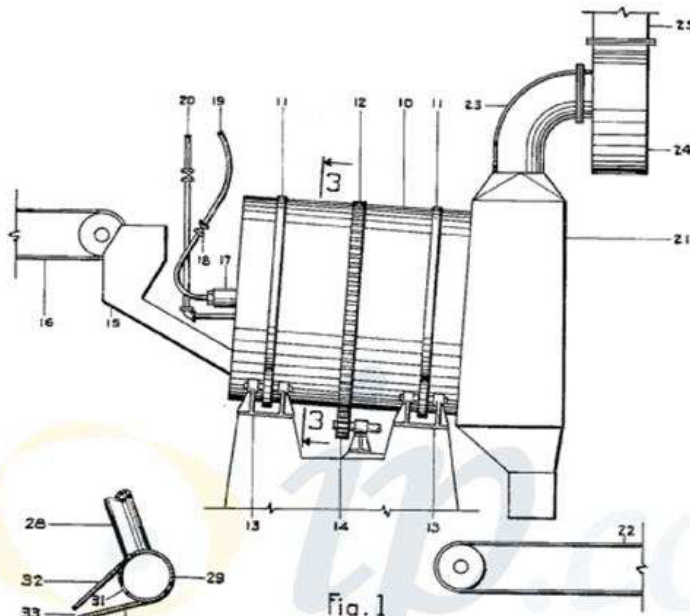
April 10, 1956

F. T. NIELSSON

2,741,545

APPARATUS FOR AMMONIATION OF SUPERPHOSPHATE

Filed Nov. 18, 1953



Francis T. Nielsson INVENTOR.
BY Bentley C. Morrow
Attorney

Figure 3 : Apparatus for ammoniation of superphosphate

3. From the 1960's to date

The changes to processing techniques since the 1960's have been evolutionary rather than revolutionary. I have the following memories from when I first started out in the fertilizer industry back in 1975 in the U.K. The plants that we operated were old, probably dating back to the 1940's and 50's.

3.1. *Materials of Construction*

A lot of wood was used, especially for floors and roof beams etc. Today practically no wood is used for any purpose – steel and concrete have taken over as cheaper and superior materials. Not much stainless steel was in evidence – rubber, and, where appropriate, brick lining, on carbon steel was employed. As better stainless steels have become available, these have tended to replace lined carbon steel in many duties due to lower maintenance costs.

3.2. *Product Size*

At the time our focus was on maximizing capacity rather than maximizing product quality. Standard product size was maybe 85% between 1 and 4 mm. Today's customer requires a much tighter and larger size specification to optimize distribution of the fertilizer by mechanical spreaders. Typically a size distribution of 95% between 2 and 4 mm is required.

This has become a practical proposition as the available screening machines have improved considerably. The machines that we operated when I first started work were essentially horizontal, frame vibrated machines with no in-built mechanism for keeping the cloths clean. The cloths tended to blind quite quickly leading to progressively more and more fines in the product. As a result we actually had an operator with a long handled brush whose job it was to physically clean the screens ("the screen man")! Luckily the current generation of screens that are available are inclined at some 35deg. to the horizontal, have static frames and the cloths are directly vibrated by electric motors, meaning that they are, to a large extent, self-cleaning.

3.3. *Control Systems*

The plants that we operated back in 1975 had a very rudimentary measurement and control scheme. Such controls, as there were, tended to be operated in manual under the control of the operator who patrolled up and down the "control panel", which consisted of a few very large dials and some knobs.

All the plants that I now work on have very much more control and instrumentation managed through a DCS with a rigorous, built-in safety shutdown system.

3.4. *Environmental Issues*

The plants that I worked on at that time either had no dedusting system or at best only a very rudimentary system to keep the working environment clean. Modern plants are designed with dedicated dedust systems with suction applied at all materials handling transfer points.

In general there have been giant strides in the HSE area.

Scrubbing systems were also very rudimentary – often, single stage scrubbing in simple void spray towers. Modern plants now typically involve three stages of scrubbing. The first two stages employ phosphoric acid as the scrubbing medium – the so-called dual mole ratio system consisting of a low pressure drop duct-cyclonic scrubber operating at a mole ratio of about 1.5 and higher pressure drop venturi-cyclonic scrubbers operating at a mole ratio of about 0.7. The last stage is typically a cyclonic tail gas scrubber utilizing water acidified with sulfuric acid to recover traces of fluoride, ammonia and particulate. All of these scrubber liquors are recycled back to the process via the preneutralizer.

3.5. *Plant Size*

The plants that I worked on back in 1975 had capacities of 25 t/h or even less and were designed to serve the market area around the plant. At that time we operated at eight plant sites and that was in a small country like England! World scale capacities have increased five-fold and product is now routinely transported in bulk by ship to global markets.

Figure 4 below has been generated from the Jacobs Granular Fertilizer Reference List and clearly shows the upward trend in daily capacity.

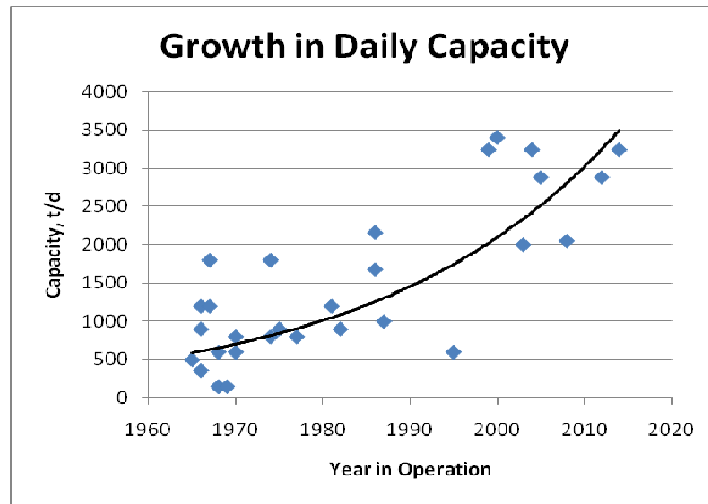


Figure 4 : Growth in Daily Capacity

3.6. Pipe Reactors

Conventional tank reactors have in many parts of the globe been replaced by so-called pipe reactors. Pipe reactors are located directly in the granulator and do not require pumping of the reaction products. This allows them to operate at high pressure and temperature and therefore the slurry produced can have a lower water content. In theory this allows a reduction in recycle ratio provided the slurry from the pipe reactor can be spread evenly on the recycle material.

My belief is that the advantages of pipe reactors are a little over-hyped. From the many plants that I have visited, I don't see many of them operating at a recycle ratio much lower than can be achieved in a well-designed and operated preneutralizer plant. Also, none of the large world-scale plants in the U.S., North Africa or Australia of 120 t/h and more are employing pipe reactors.

4. The future

I believe that the definition of a world-class DAP plant will continue upwards – the 5,000 t/d DAP plant is just around the corner. Actually, I am confident it could be designed right now.

Environmental standards will continue to be tightened up and scrubbing systems will continue to evolve to meet those new standards.

Product quality – meaning closer control of chemical and physical quality (tighter and tighter size specifications, a demand for increased sphericity and improvements in anti-caking treatments – will continue to be a focus point.

The production of specialty fertilizer containing micronutrients will grow. Following the tightening of environmental emission standards worldwide and the consequent reduction of acid rain, soils are becoming deficient in sulfur. I expect sulfur enhanced fertilizers to become a growth market

And lastly, I believe that granulation plant control systems will become more intelligent, taking a lot of decisions away from the operator to be determined by computer. This will in part assist in achieving the advances mentioned above.

In summary, we've come a long way since we started crushing up bones and solubilizing the phosphate by adding sulfuric acid in batch pits!

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