Gas Purification

Gas Manufacture: Note 1_{v1}

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Introduction

Once the coal tar and ammoniacal liquor had been removed from gas through various pieces of plant such as the hydraulic main, foul main, tar tower, condenser, washer, scrubber, tar extractor and electrostatic precipitator, it was then important to remove the remaining impurities in the gas. These are namely hydrogen sulphide and hydrogen cyanide, these two impurities in the gas had to be removed as they greatly increased the risk of poisoning and they were removed by a process called purification.

The Purification of Gas

Samuel Clegg first experimented with lime purification at the home of Henry Lodge of Sowerby Bridge (Clegg had previously lit the mill belonging to Henry Lodge), Clegg placed lime within the water in the base of a gas holder, however it was not a great success, later at a works he installed in Coventry Clegg developed a paddle system to agitate the lime. By 1912 Clegg had developed a separate tank which contained a wet lime based purification system. This system was incorporated in the small gasworks built by Clegg for the Soho publisher Mr Ackerman and is shown in the picture to the right of the apparatus as it appeared in Frederick Accum's first book on the science of the Manufacture of Gas.
The Wet lime purifier was developed and improved upon by Clegg, Malam and others. The better known Dry Lime Purifier did not appear till later. The first work on a dry lime purifier was undertaken by Reuben Phillips of Exeter, for which he received a patent.

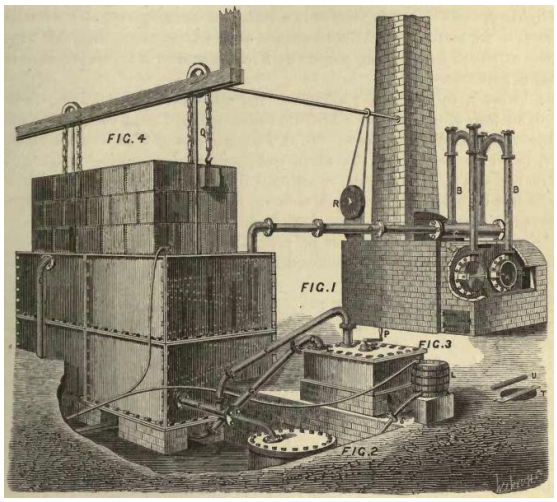


Figure 1, The Gasworks built by Clegg for Ackerman, indicating the retort setting (FIG. 1), tar receiver (FIG. 2), Lime Purifier (FIG. 3) and Gasholder (FIG. 4).

Mr Philips purifier was in many ways similar to the traditional system employed later on in most gasworks as it work on the basis of forcing the gas through layers of hydrate of lime, but it was flawed and the benefits not realised until his patent had expired. The main driver for the replacement of the wet lime system was not performance but issues with the disposal of the "foul lime" known as "Blue Billy", the blue pungent waste created from the process, which caused problems for the gas companies to dispose of. Wet lime was then superseded in most situations by the use of dry lime purification.

The design originally produced by Reuben Philips had been flawed through lacking a bottom and just sealed with water and issues with the design of the pipework. This was later rectified by ensuring the unit was sealed on all aspects, including the removable lid and that the gas was passed through the grid in a sequential manner. The dry lime purifier was in fact an incorrect term, as the lime was in reality moist hydrated lime, a purely dry lime would not have reacted with the impurities in the gas. Lime of the highest quality had long been (and still is) available for quarries in the UK, most notably from Buxton Derbyshire.

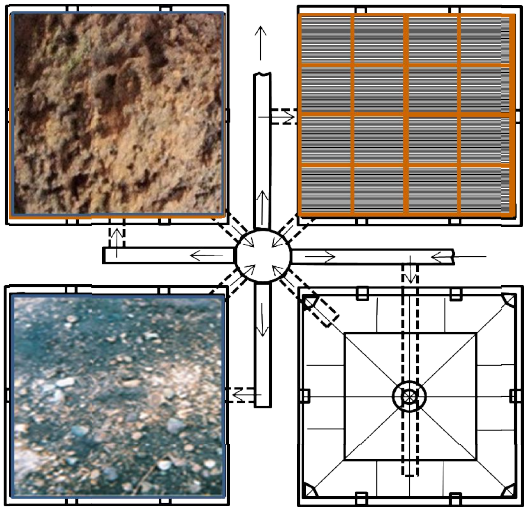
Lime was later replaced in most gasworks by bog iron ores, these ores came from naturally occurring peaty deposits of iron oxide found in large quantities in Ireland, the Netherlands and Belgium, some locally sourced deposits were found in England mainly around the town of Westbury in Wiltshire. In its natural form the ore contained between 50 to 60% water, between 30 to 35% ferric oxide (Fe_2O_3) and an additional 15 to 25 % of organic vegetable matter and inert silica base mineral). Although bog iron ore superseded the use of lime, lime was still used in combination with bog iron ore for purification purposes.

The Purifier

The purifier was typically a rectangular box constructed of iron, steel or occasionally concrete. Within these boxes were arranged grids usually of wood covered in the lime or bog iron ore superimposed in layers vertically through the box. The lime or bog ore would be laid on the wooden (often oak) grids inside the boxes in layers 12 inch to 18 inch deep, sometimes with lime mixed in with the bog iron ore.

The gas would flow from the inlet to the outlet so that the gas would contact with all the lime or iron ore. The purification boxes were normally laid in duplicate so that when the efficiency of one set of purifiers dropped they could then be switched onto a second set. On large gasworks this concept was expanded further by building purification units of a much greater size both in rectangular and cylindrical format. Typical box purifiers can be seen in Figure 1, showing purifiers set out in a cluster of 4 purifiers in a square fed from a central valve and a box purifiers laid out in a row with the gas supply provide via a main running down the back of the unit.

Figure 2. (left) Box purifiers at the former Fakenham Gasworks, now a gas museum. (right) A schematic of a set of 4 purifiers, showing empty (bottom right), wooden grids (top right), filled with bog iron ore (top left) and spent oxide (bottom left).



The Chemistry of Gas Purification

The main role of the purifier was to remove two key components from the gas, namely hydrogen sulphide (the largest impurity) and hydrogen cyanide. Hydrogen sulphide accounted for roughly 1% of the total volume of the unpurified gas; it was present at an order of magnitude greater concentration than hydrogen cyanide, which accounted for 0.1% of composition of the unpurified gas. These were not the only impurities in the gas; others would have been present such as trace amounts, such as thiocyanate salts, carbon disulphide, ammonium salts and coal tar. It should also be highlighted that some of the soluble forms of cyanide, such as ammonium salts of cyanide would have been removed prior to the purifier, through the action of the washers and scrubbers depositing the cyanide compounds in the ammoniacal liquor. Ferrocyanide salts would also be present in the spent liquor from an ammonium sulphate plant often found on larger former gasworks.

Lime purification

Gas was originally purified by passing it through wet lime; however this was later superseded by dry Lime processes. As wet lime processes were phased out relatively early on their chemistry will not be discussed further, although there are obvious similarities to the dry lime process, which used hydrated lime.

Lime purification used hydrated lime otherwise known as calcium hydroxide $Ca(OH)_2$. During lime purification of coal gas hydrogen cyanide would be removed as calcium thiocyanate ($Ca(SCN)_2$)) and to some extent as calcium ferrocyanide, $Ca_2Fe(CN)_6 \cdot 12H_2O$.

$CaH_2O_2 + H_2S = CaS + 2H_2O$

The Calcium sulphide formed reacts with carbon dioxide in the gas through the following reaction.

$CaS + CO_2 + H_2O = CaCO_3 + H_2S$

The gas then passed into a second purifier box where the initial reaction would occur again.

$CaH_2O_2 + H_2S = CaS + 2H_2O$

As can be seen from above the lime also removed carbon dioxide from the gas, predominantly in the first purifier box. Once the capacity of the lime to remove impurities from the gas started to diminish significantly, the gas would be diverted to a duplicated set of purifiers to be purified. The contents of the purifiers would then be dug out and left to weather in the air, once weathered the lime could be reused again a couple more times until saturated with sulphur and cyanide.

Bog Iron Ore Purification of Gas

Bog iron ore in its natural form contained between 50 to 60% water, between 30 to 35% ferric oxide (Fe_2O_3) and an additional 15 to 25 % of organic vegetable matter and inert silica base mineral). When the hydrogen cyanide present in coal gas was passed over bog iron ore it would predominantly form Ferric Ferrocyanide Fe_4 $[Fe(CN)_6]_3$ also known as "Prussian blue", the complexity of cyanide chemistry is such that many other forms would have been present albeit at lower concentrations. This intense “Prussian Blue” colour is what gave spent oxide its distinctive colour.

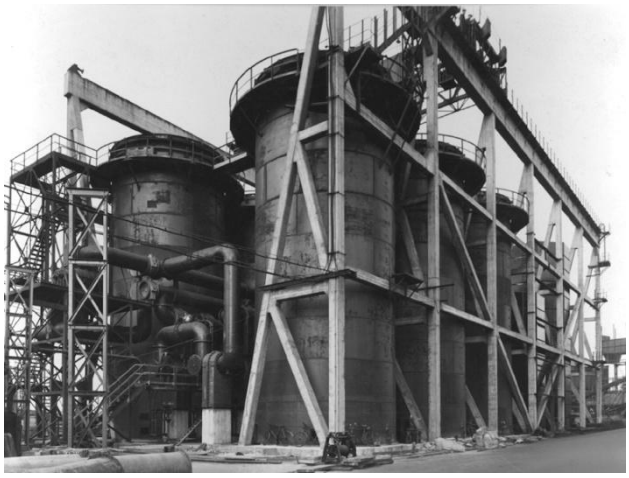


Figure 3. Tower Purifiers on a large gasworks.

For sulphur removal the ferric oxide in the bog iron ore would react with the hydrogen sulphide forming ferric sulphide and releasing water, in addition another reaction between ferric oxide and hydrogen sulphide would form ferrous sulphide and sulphur and water. These chemical reactions are shown below:

$Fe_2O_3, H_2O + 3H_2S = Fe_2S_3 + 4H_2O$
$Fe_2O_3, H_2O + 3H_2S = 2FeS + S + 4H_2O$

As with lime purification once the capacity of the bog iron ore started to diminish significantly then it needed to be revivified by exposure to air, this would normally be achieved by digging the oxide out by hand on to a covered revivifying area. As the oxidation reaction which would occur by exposing the highly reduced oxide to air was exothermic and the sulphur combustible, the oxide would occasionally spontaneously combust, making this operation quite hazardous. During revivification the ferric and ferrous sulphides would react with water to reform ferric oxide and sulphur through the equations below:

$2Fe_2S_3 + 3H_2O = 2Fe_2O3 + 3S_2$
$12FeS + 9H_2O = 6Fe_2O_3 + 6S_2$

This revivification process could be repeated 2 to 3 times before it became spent, forming the well known by-product/waste called “Spent Oxide”.

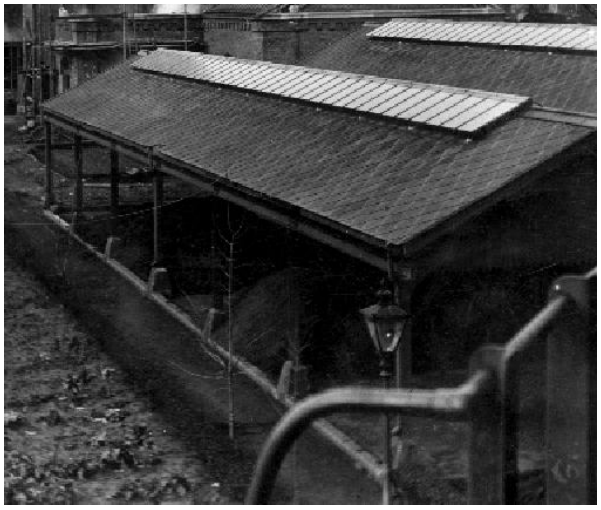


Figure 4. A shed used for the revivification of spent oxide.

Figure 5 . A concrete built purifier house.

Foul Lime and Spent Oxide

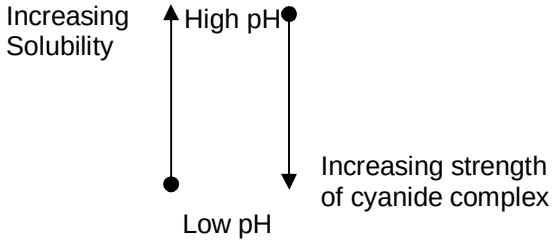
Foul lime was a greenish white cementitous substance often found to be similar to a weathered cement when encountered on a former gasworks. The material was very alkaline as you may expect from its predominantly lime composition. Once weathered the foul lime was a very effective fertilizer and disposal was not usually a problem and the material was often sold for such purposes.

Spent oxide was used for the manufacture of sulphuric acid, it could be roasted in a Herrishoff furnace like sulphur rich ores such as iron pyrites, with the resulting sulphur dioxide gas collected and used for the acid manufacture. The Prussian blue colour was also used as a dye in the textile industry and also as eye shadow. Spent oxide was often used as a weed killer a practice often carried out on former gasworks. These markets disappeared in the early part of the 20th century and the material then had to be disposed of as a waste.

The cyanide present in spent oxide forms up to 6% of the total weight and is predominantly in the form of complex metal cyanides and thiocyanate. Spent oxide also consists of about 3-9% iron, 0.08-0.36% manganese, 2-3% sulphate and 36-60% free sulphur. The predominant iron cyanide complex is insoluble iron ferricyanide also known 'Prussian Blue', a stable and highly insoluble form of cyanide with a pH of about pH4.

$Fe_4[Fe(CN)_6]_3$
Iron Ferricyanide
Insoluble

The potential for cyanide to infiltrate groundwater is dependent on the behaviour of iron ferricyanide, which is dominated by the pH of its environment. Under the acidic conditions (pH4) which usually occur in spent oxide it is highly insoluble, reducing the leaching of cyanide into groundwater.



The acidic conditions predominate due to sulphur oxidising bacteria, which slowly convert the sulphur in spent oxide to sulphuric acid. However, if the pH exceeds pH 6, then iron ferricyanide starts to dissociate into hexacyanoferrate.

$Fe(CN)_6$
Hexacyanoferrate
Soluble

Hexacyanoferrate can dissociate photolytically when exposed to light, albeit slowly, to release hydrogen cyanide and iron. The released iron can then bind with hexacyanoferrate driving the equilibrium back towards iron ferricyanide formation. If spent oxide is mixed with alkaline substances such as cement then it has the potential to release the soluble hexacyanoferrate complex into ground and surface waters under the right conditions. Hexacyanoferrate can be highly mobile in water and potentially toxic to aquatic life forms as well as endangering drinking water.

Figure 6. Spent oxide staining on a wall (left) and a patch of spent oxide (right) both on former gasworks.

Foul Lime and Spent Oxide may be found in the ground near the purifiers and land used to revivifying the spent material. They may also be found anywhere that ground levels have been made up.

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