Production Of Hydrogen by the Steam-Iron Method

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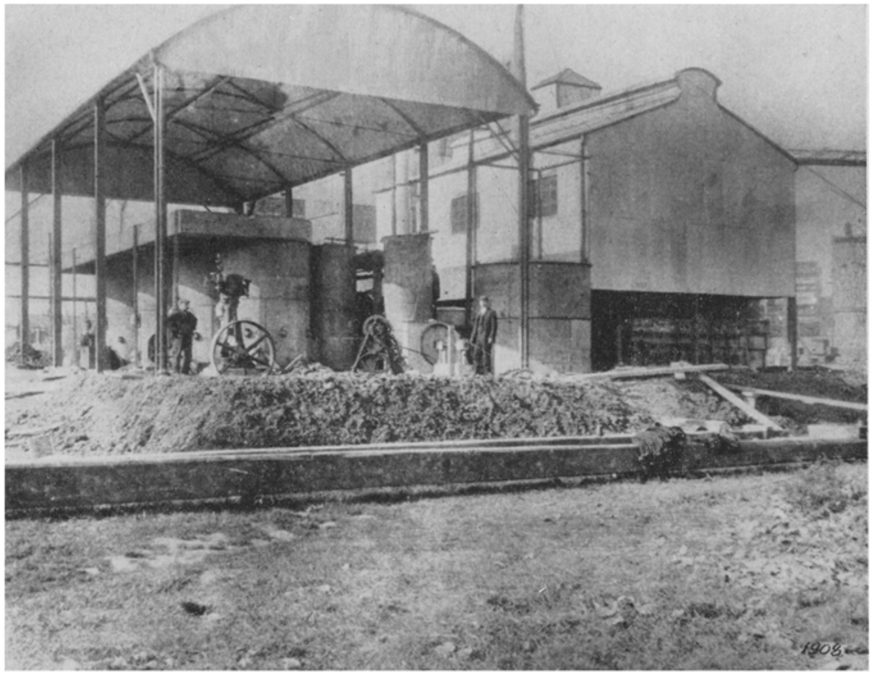
Brief History of the Development

A SEARCH of the literature discloses various attempts at producing hydrogen, using steam and iron, were made before 1900[a] but there is no indication that any of these developed into successful commercial production. In 1903, Howard Lane (an engineer in Birmingham, England) devised an apparatus which has been very satisfactory, and all designs used in the present day owe their beginning to the efforts of Lane. In those early days there was a great demand for large volumes of cheap hydrogen for use in inflating military balloons and zeppelins which were just being developed.

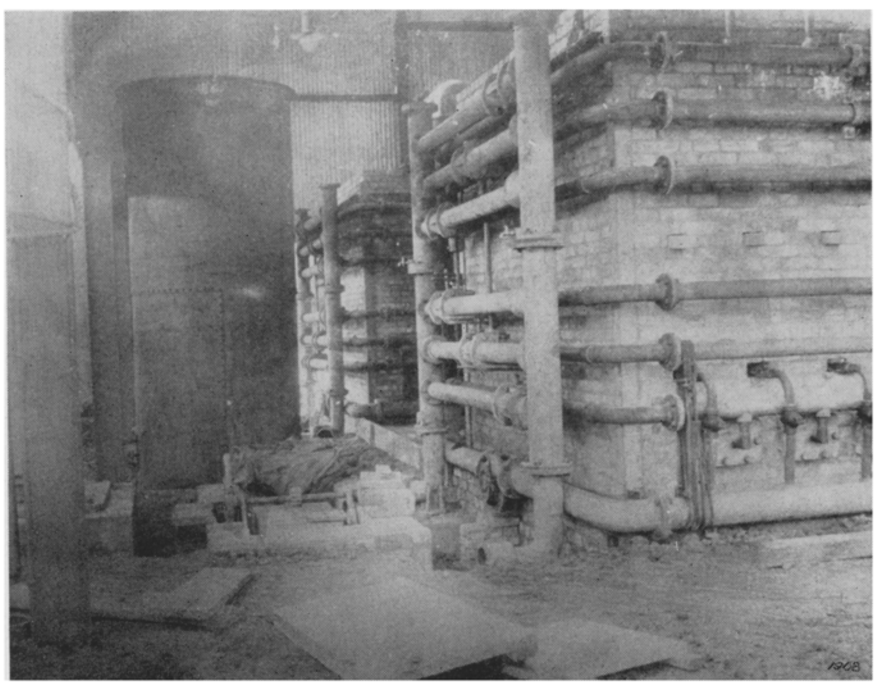
After some trying experimenting, Lane's first commercial unit was ready and erected at the St. Louis Exposition in 1904, being used successfully to inflate the balloons which started from the fair grounds in the Gordon-Bennett race of that year. The plant was awarded a silver medal for scientific achievement. After this, Lane supplied plants to most of the powers of Europe for military use, and strange as it may seem, Russia was the first power to build a plant. It was about 1908 when the first plant was built for industrial use in the oil industry, and many were the troubles and disappointments with this installation. Industrial requirements of 24 hours a day, 7 days a week and high purity, at a price, were far different from running a plant during army maneuvers lasting two weeks, and where entire regiments of men were available to clean fires and change purifiers. These plants never ran long enough on continuous production to exhibit their shortcomings, so the first industrial plant inherited all the troubles.

About 1910, other interests became concerned with the building of steam-iron plants, and on the Continent, many of Lane's ideas were copied for a time, only to find his mistakes had been incorporated in their designs. Naturally, these plants were not successful.

(a) Joseph Jacob B.P. 593-1861, Gifford in 1878, Lewes in 1890-1891 (H. S. Taylor — Industrial Hydrogen)



Lane Plant under Construction



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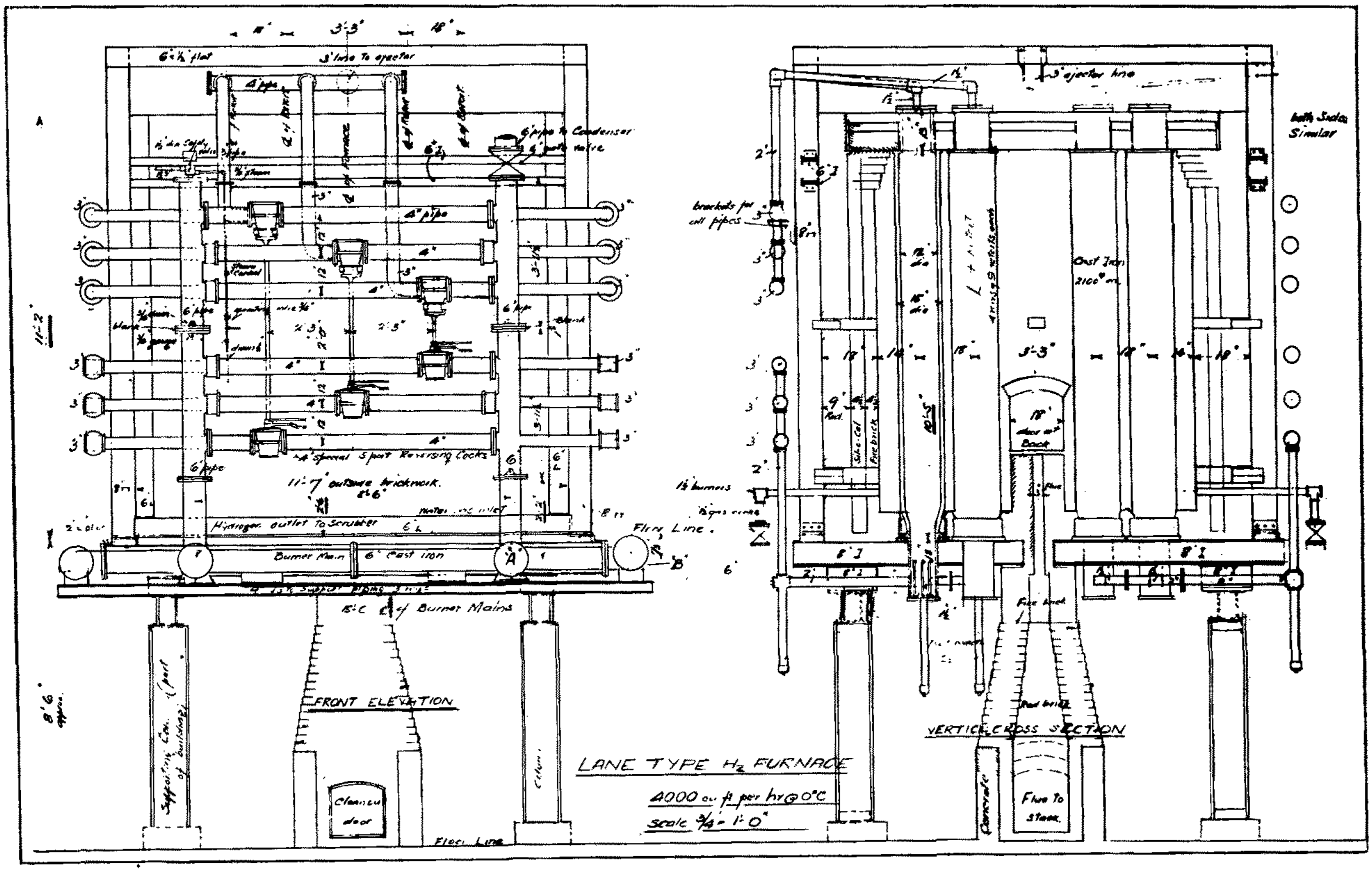

Plate I.

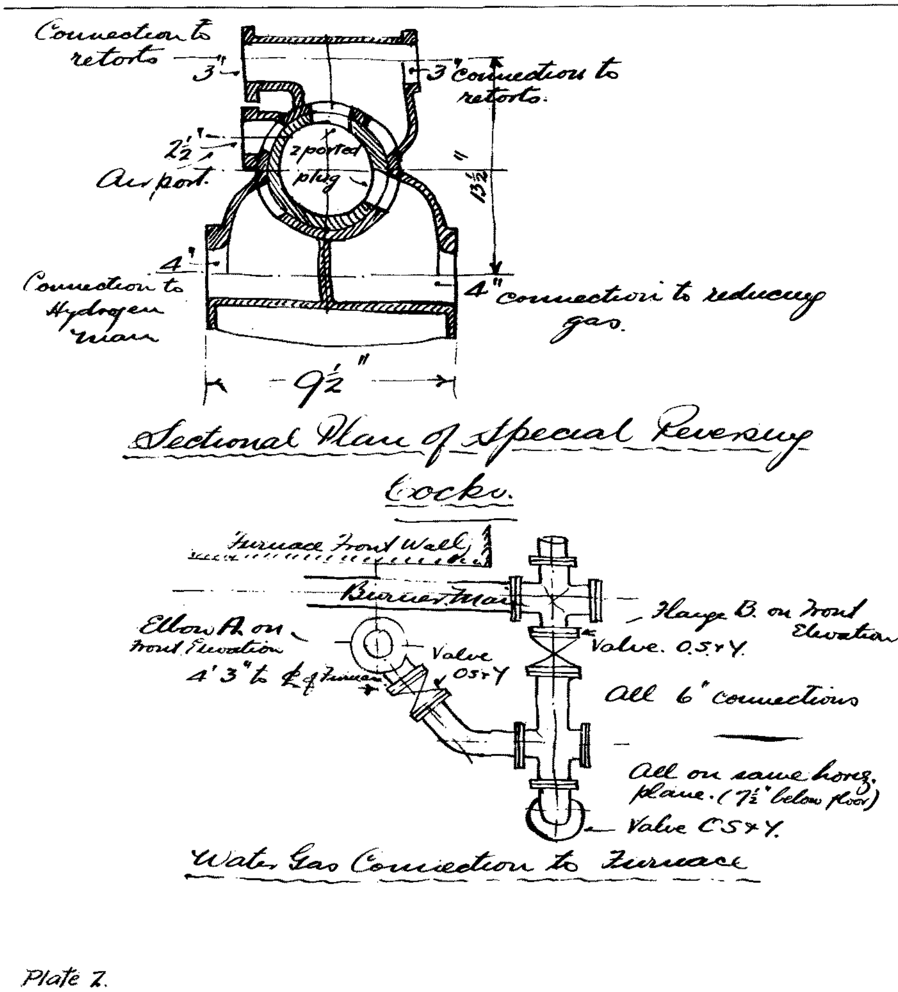

Plate 2.

Plants of this type were erected in the United States and had much to do with creating a bad impression regarding steam-iron plants. It was a misnomer to call them Lane plants. (A properly managed modern Lane plant is still highly successful in respect to gas purity, but cost is a drawback.)

I do not have definite information as to the total number of successful plants installed by Lane, since my association with him covered only the period of 1903-1913, but he continued in business until his death about 12 years ago. In 1921, I met him in London and he told me that the designs we conceived in 1912 were still good and business was satisfactory.

The author personally had the job of design, field erection, and starting up of all Lane plants from 1907 to 1913 and since then has built a number of those plants which were all successful in industry, representing a total potential production of 850,000,000 cu. ft. hydrogen annually.

About 26 years ago, Doctor Messerschmitt introduced a different type of hydrogen generator which eliminated the use of multiple retorts used by Lane and reduced the cost of the apparatus and maintenance cost. This design is in use very successfully in many countries.

Very soon after Messerschmitt, there came a modification of his design, embodying the same basic principles but mechanically different. This is known as the Bamag plant, and it would be difficult to say very accurately whether there are more of this type than Messerschmitt's or vice versa in successful operation today.

There are other designs registered in patent literature which apparently have not been marketed, so it is deemed unnecessary to discuss them here, since at this meeting there is little interest in designs that have not been proven.

The Process

So much has been written on the subject covering the reactions involved and the theoretical heat balances that further repetition here is not essential. Sufficient for the purpose, the main reactions may be stated: — Iron, at the proper temperature, when a flow of steam is passed over it takes up oxygen which forms iron oxide and liberates hydrogen. This reaction, carried on until the iron cannot take up any more oxygen, ceases, and it is necessary to stop steaming and regenerate or reduce the oxide to the metal by passing water gas over the iron oxide.

If it were possible in commercial plants to produce reducing gases composed only of CO and H_2 the troubles of designers and operators would be over. Since water gas is the best reducing gas available, and coke is the fuel, there is always the problem of sulphur to overcome. Also, the volatile content in the fuel has to be reckoned with.

In addition to the reactions mentioned, there are those formed by iron, sulphur, and carbon during reduction and on the steaming phase reactions between hydrogen, sulphur, carbon and oxygen, which produce some simple and other complex compounds.

It has been a problem to incorporate in gas generator design a means by which the operator may prevent much of the undesirable compounds being formed.

Types of Commercial Plants

There are two distinct types of hydrogen generators using the steam-iron system: (a) the multiple retort known as the Lane type, (b) the single retort known as the Messerschmitt and the Bamag type.

The Lane type (plate No. 1) consists of a battery of usually 36

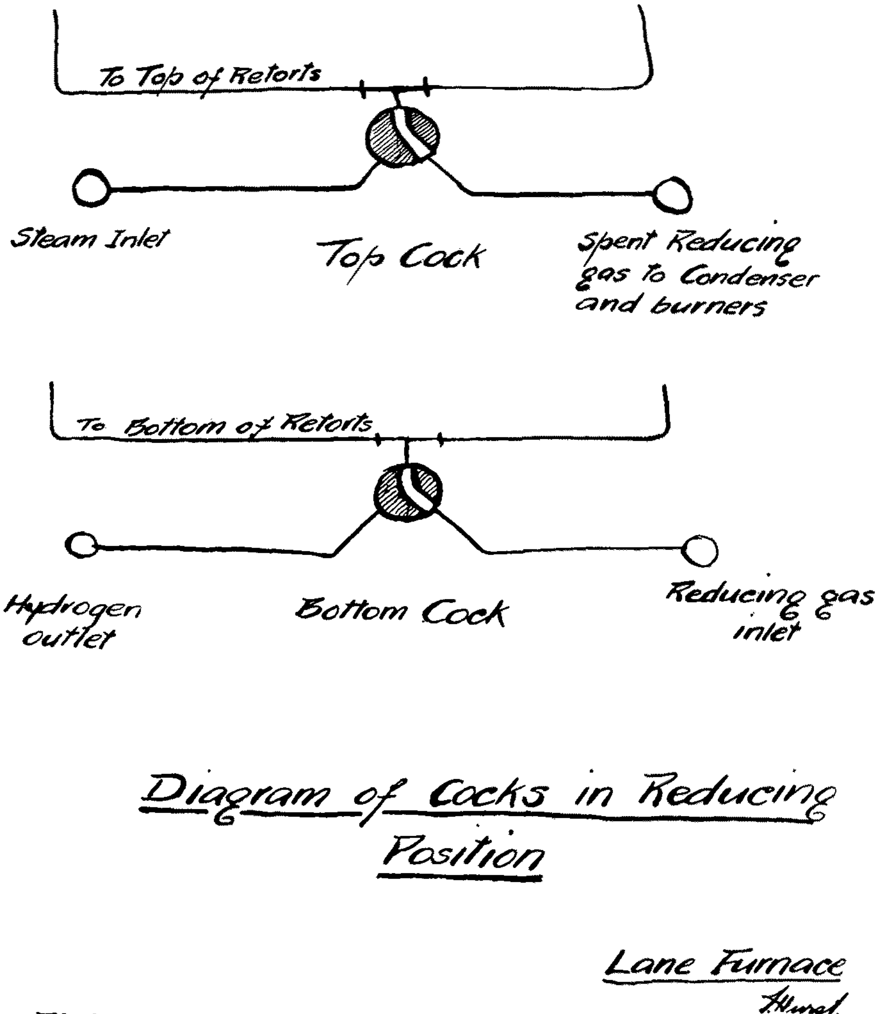

Plate 3

vertical retorts set in a brick furnace chamber heated by gas burners arranged on each side. The retorts are grouped into 3 sections of 12 retorts each and these sections are connected to a pipe frame in front of the setting, which acts as the operating stand. Each section has two operating cocks, one top and one bottom which guide the flow of reducing gas, steam, air, hydrogen, and spent reducing gas. A section of one of these cocks is shown on plate No. 2. The arrangement of these cocks allows the reducing period to be twice the length of time of the steaming period; it also allows a very simple control of the blowing or "burn off" period. Plates 3, 4, and 5 show in diagram form the respective positions of the plugs in the controlling cocks during reduction, steaming, and air blowing.

To charge ore into the retorts, the top flanges are removed, and to discharge spent ore, both top and bottom flanges are removed. Suitable dust pockets are provided at vulnerable points in the system.

Spent reducing gas passes through a condenser to remove steam formed during reduction; the gas then is burned on the outside of the retorts to maintain operating temperatures. The hydrogen made is scrubbed, measured, purified of H_2S and CO_2 and piped to the storage holder. All reducing gas is purified of H_2S before reaching the retorts.

The Messerschmitt Generator

Plates 6, 7, and 8 show very graphically the construction and three phases of operation, these illustrations being of one of the early designs. A later design is shown on plate 9.

Referring to plate 6, the generator is a steel shell lined with specially shaped refractories and fitted with 2 metal cylinders, one inside the other. The space between these cylinders forms the retort or ore bed. The centre cylinder is filled with refractory checker work. Reducing gas, air, and steam connect with the bottom of the inner cylinder and additional air connects to the superheater on the outside

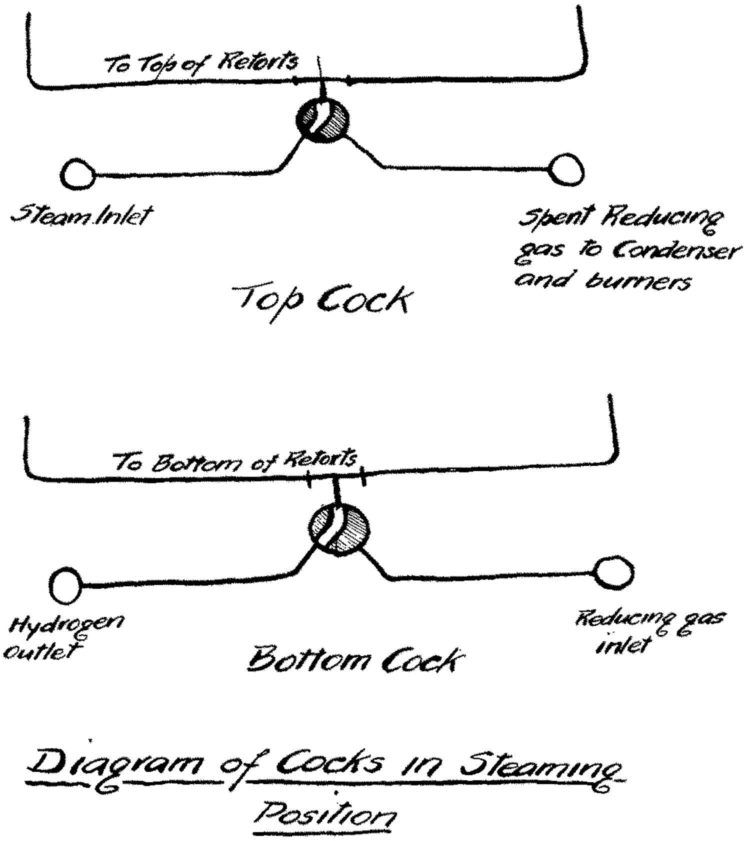

Plate 4

Lane Furnace
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of the larger cylinder. An outlet for hydrogen, a stack valve and a steam inlet, together with charging and discharging doors complete the mechanical attachments. All valves are properly interlocked with operating mechanism to make operation positive and safe.

A later design, shown on plate 9 is provided with only one central cylinder, set within a refractory lined shell; the space between the cylinder and shell lining forms the retort. All the other required connections are provided in the regular manner, as will be seen from the diagram. Reducing gas is used raw, i.e. no purification of H_2S. Purification of hydrogen is the same as in Lane's system.

The Bamag Generator

Plate 10 shows the essentials incorporated in the design of this type generator. This consists of a steel shell lined with refractory brick with a specially designed combustion arch about 2/3 of the depth of the generator above the grate. Above this arch is a chamber filled with checkers which acts as a superheater for steam when making gas, also during the initial heating period. The lower chamber between grate and arch is the retort or ore chamber. At the bottom of this chamber, connections are made for reducing gas inlet, hydrogen outlet, and a purge line. In the

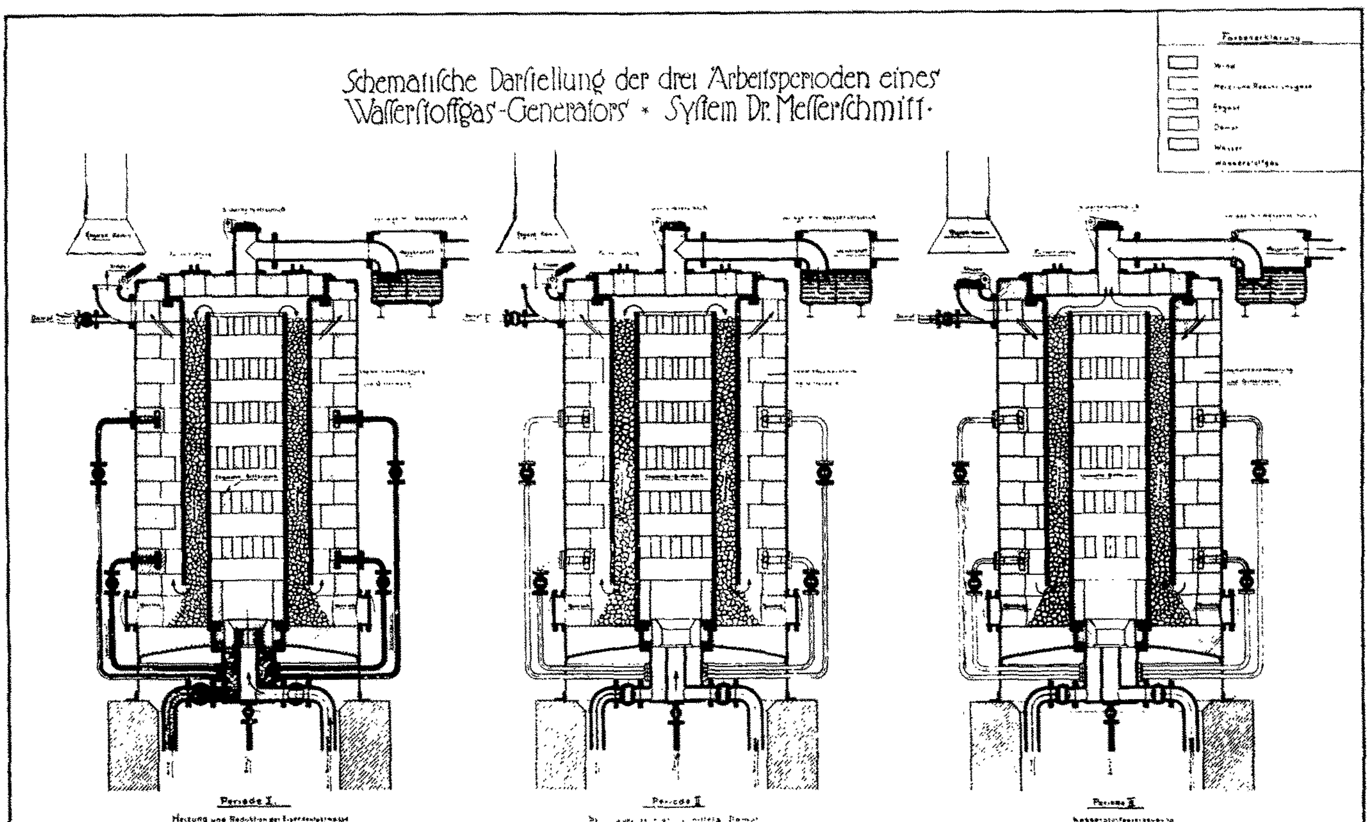


Plate 6 Plate 7 Plate 8

upper portion of the combustion arch, an air inlet is provided for combustion of gas after leaving the ore bed, and another air valve is fitted just below the stack valve for use as a "burn off" air supply.

Steam enters the top of the superheater just below the stack valve. Suitable charging and discharging doors are provided. All valves are operated from an interlocking mechanism similar to the one previously mentioned.

The reducing gas is used without purification, but the hydrogen is purified of H_2S and CO_2 as in other systems.

Impurities

The greatest source of trouble in operation of a steam-iron plant is sulphur compounds, and these of course originate from the sulphur content of the fuel used for producing water gas. Therefore, in deciding on the coke to use, much consideration should be given to its sulphur content. In some plants the water gas is purified by removing H_2S before the water gas is used as the reducing agent, but in the majority of installations, the water gas is used not so purified. The chief advantage of the removal of H_2S is that the ore mass has a much longer life and the final H_2 purifiers do not have as much work to do as in the latter case. After removal of H_2S from the raw hydrogen in both instances, the purity of the gas is equal, in terms of sulphur content, and the economics of manufacture are in favor of the latter method. Also, from a safety standpoint the elimination of water gas purifiers removes from the plant the most hazardous operation in the plant, i.e. the possible danger of exposing men to the toxic effect of CO when working on purifier boxes.

Each reduction period adds some sulphur and carbon to the contact mass, and each make or steaming takes some sulphur compounds away, also some carbon as CO, CO_2; but these two elements, sulfur & carbon, are not released by the contact mass as quickly or as easily as they are absorbed by the contact mass from the reducing gas, and a building up or accumulation of sulphur and carbon by the iron mass is the result after many hours of operation, and is indicated by analysis.

If this accumulation is allowed to continue, it may result in an almost complete refusal of the contact mass to decompose steam. This statement may be considered by many as mere speculation, but it happened to the author before the necessity of what we now know as "burning off" was discovered.

To avoid undue accumulations of sulphur and carbon on the contact mass, means are provided in all makes of generators for drawing air over the mass at regular intervals. In plants using purified reducing gas, one air blow or "burning off" each 4-hour period is sufficient, the air blow lasting 10 minutes, and in those plants using unpurified reducing gas, it is attempted for a few seconds in each cycle.

It was the discovery by the author of the necessity for this air blow or "burn off" that gave the Lane plant its place in industry in the early days and today it is that same feature which makes possible the control of purity of the gas produced by any make of steam-iron generator.

Since the majority of steam-iron plants in this country are of the single retort type, a comparison of the operation of Messerschmitt and Bamag designs may be of interest. (See bottom of page 34)

Observations

Mention has been made of the importance of the air blow in both productivity and hydrogen quality, and on analysis of the foregoing tabulation of the features embodied in the Messerschmitt and Bamag designs, it would appear that these designs had provided for this feature in the regular cycle. However, when it is considered that the air for the "burn off" is high temperature, due to passing through the superheater before reaching the ore, and that heat is developed in the ore bed by oxidation as air is blown through the bed, it is very easy to ruin the condition of the ore by a blow of any length of time, and the purpose of the blow is often thwarted due to a rapid rise in ore bed temperature, before the oxygen has had time to perform the required function and the air blow has to be stopped short. It is therefore a very essential duty of the operator to lower the temperatures for a while previous to an

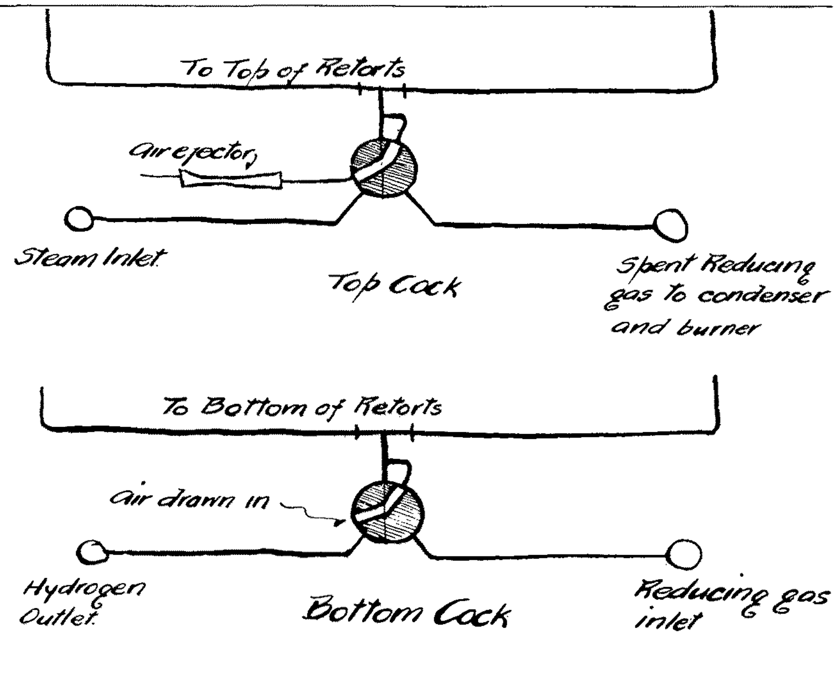


Diagram of Cocks in Blowing Position

Plate 5

Lane Furnace

Hurst.

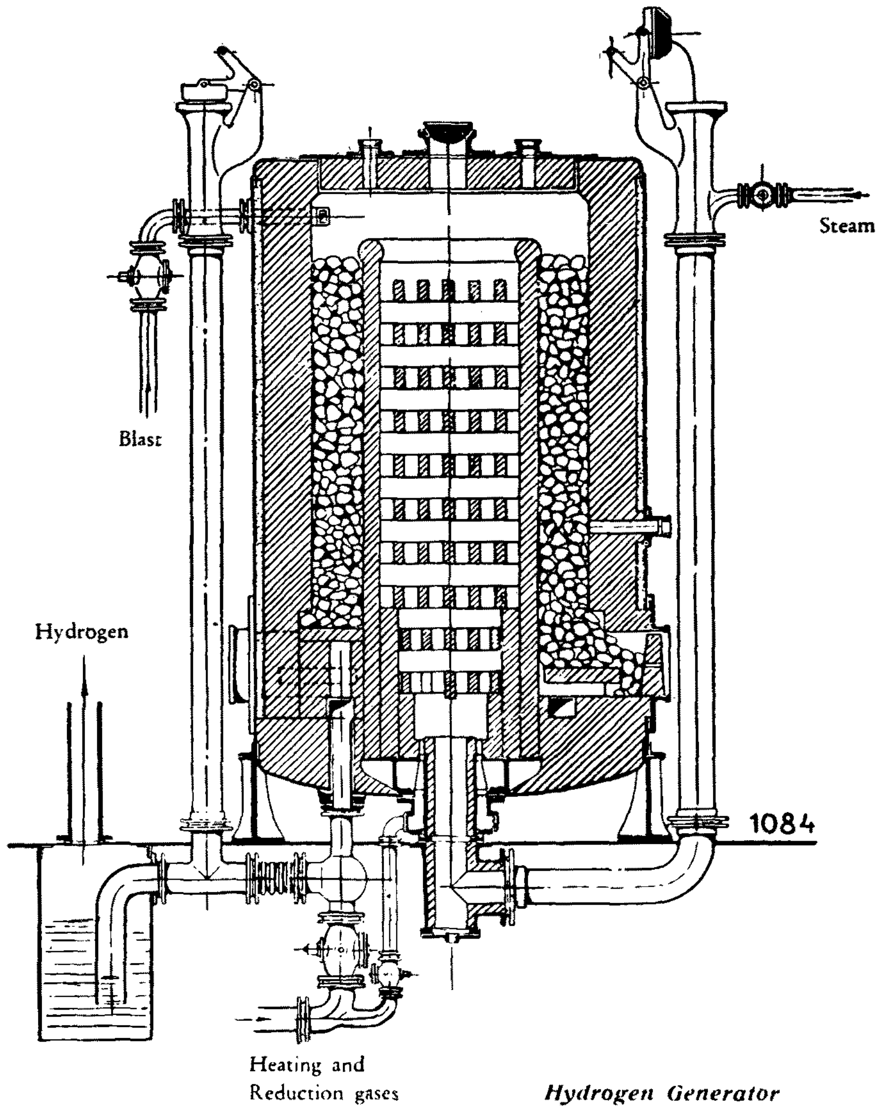
extended blow period so that a sufficient length of blow will perform its work and not raise the ore bed temperature more than about 60° F. above normal operating temperature. This rise should be no cause for alarm since the first reduction after the blow will pull the temperature down very rapidly because of the rapid reduction which is an endothermic reaction. Cooling a set for the blow is a simple matter, calling only for a reduction in air for combustion in the superheater resultng in a drop in superheater temperature.

Contact Mass

Many forms of iron have been used as a contact mass with more or less success, ranging from crude iron ores to steel turnings. The ideal material for this purpose would contain sufficient iron to give capacity, with a suitable binder that would render the mass porous and at the same time be sufficiently strong to maintain its shape for a reasonable time, disintegrating very slowly. The binder should be very free from fluxing characteristics and as near as possible inert to the reaction gases. The hematite ores are not successful, and after many trial runs the low grade ores have been most satisfactory. Included in this class are some Virginia ores, Alabama brown ores, lump pyrites cinder, and some European ores of the iron carbonate group. Ores with small amounts of copper and/or manganese give evidence of greater activity and higher purity of gas made than those that are free from these elements. It is of course desirable that the mass be free or nearly so from sulphur which of course is not the case with pyrites cinder. This material is especially active as a contact mass but its initial sulphur content and subsequent affinity for sulphur, together with its lack of strength, make it the least desirable form of iron to use.

Man-made briquettes have been tried with very little success and to date the natural ores are the most dependable materials to use. The early plants used heavy steel turnings packed into retorts, and satisfactory results at that time were obtained. However, the water gas-hydrogen ratio was high and the need for a more efficient material led to the use of lump pyrites cinder. Natural ores came into use about 26 years ago and a large proportion of present day plants continue to use them.

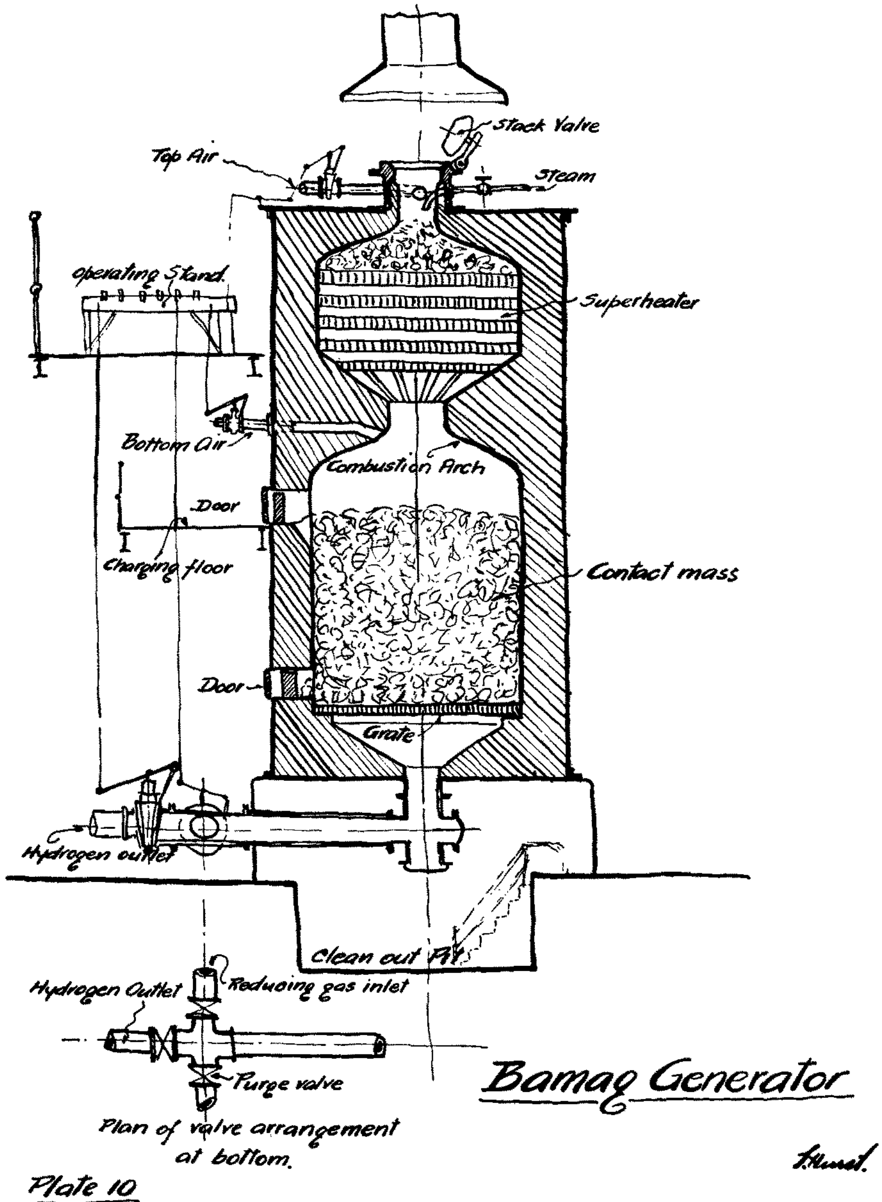
Single-cylinder



Hydrogen Generator

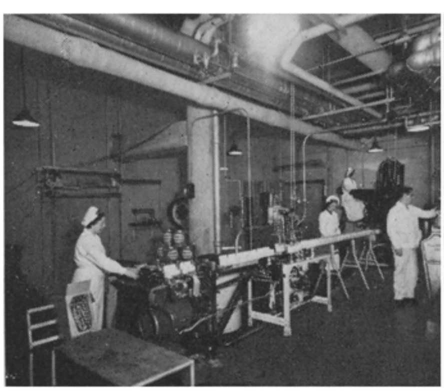
Plate 9.

	Messerschmitt (2 cyl. type)	Bamag
Heating up	Partial combustion within inner tube, sensible heat of gases passing down through ore, and complete combustion on outside of outer tube heats up the ore. Further heating is obtained by steaming and venting the hydrogen made to the atmosphere.	Cold reducing gas passes up through the ore bed, meets air below the combustion arch and heats up the superheater. Radiation from the arch and a few hours of steaming carry heat into the ore. The product of steaming is vented to the atmosphere.
Reducing	Reducing gas passes up the centre tube either alone or with a small amount of air, if desired, down through the ore, into the superheater where with additional air the gas burns and keeps up the temperature of superheater.	Reducing gas passes up through the ore and at the combustion arch meets air for combustion and keeps up the desired temperature of the superheater.
Steam Purge	Steam up in same direction as reducing gas and away to atmosphere through stack valve.	Steam through superheater, down through ore and out to atmosphere by way of purge valve.
Make	Steam through superheater up through ore bed and resulting gas out through hyd. outlet pipe.	Same as purge but purge valve closed and hyd. valve open.
Air Purge blow or "burn off"	Air through centre tube down through ore and away to atmos. by way of stack valve.	Air blow through superheater down through ore and out to atmos. through purge valve.



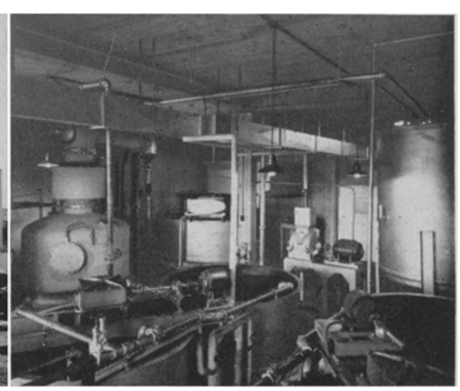
New Packing Plant

Canada Packers, Ltd.
Vancouver, B. C.



Filling Equipment

Outside View



The Oil Refinery