

**HYDROGEN PEROXIDE WORKS OF
OTTO SCHICKERT & CO.,
AT
BAD LAUTERBERG and RHUMSPRINGE**

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BRITISH INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

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HYDROGEN PEROXIDE WORKS OF OTTO SCHICKERT & CO.

at

BAD LAUTERBERG and RHUMSPRINGE

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Personnel of Team.

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Before dealing with the Factories it is desirable to record a short history of the manufacture of Hydrogen Peroxide in Germany, particularly the development of the manufacture of concentrated Hydrogen Peroxide for war purposes. The source of information is from earlier C.I.O.S. reports.

HISTORICAL.

Hydrogen peroxide for commercial purposes is usually in the form of a solution containing 35% H_2O_2 . The development in Germany of a concentrated solution of Hydrogen Peroxide containing 80 - 85% H_2O_2 as a source of power generation in connection with the jet propulsion for Rockets, starting devices for airplanes, driving of submarine turbines and propulsion for torpedoes, dates from the 1914 - 18 War to the end of the 1939 - 1945 War.

It is interesting to note that the development and manufacture of Concentrated Hydrogen Peroxide in Germany was carried out by Industry, and has chiefly been in the hands of the Electrochemische Werke, München, partly a family concern, under the direction of Dr. Albert Pietsch, 70 years of age, who was President of the Company and one of the larger shareholders, and his brother-in-law, Dr. Adolph, 65 - 70 years of age, Director Chemist.

The capital of the Electrochemische Werke is 2,000,000 RM. A dividend has been paid for the last 10 years of 6%. The shareholders of the Electrochemische Werke, München, are:-

	%
Dr. Pietsch	24
Dr. Adolph	24
Elfa Haran Aarau G. of Switzerland	13
Dr. Thoma - Zurich	4
Merck Holdz Co. Switzerland	28
Frau Kramer, Garmisch	4
Dr. Zeitelmann, Würzburg	3
	<u>100</u>

The first enquiry from the German Government for concentrated Hydrogen Peroxide came to Dr. Pietsch during the 1914-1918 World War. The production of such material was impossible at that time due to lack of knowledge of the properties of high test peroxide, especially with respect to stability and stabilisation and to lack of proper materials of construction. The result of the enquiry however was to stimulate Dr. Pietsch to a long term research programme on the subject which eventually led to a successful

process and to large scale use.

During the period 1920-39 Krupp put on the market various stainless steels, of which V-2A, V-4A and V-14A were found to be especially valuable for Hydrogen Peroxide solutions because they did not impair stability. Polished V-14 was found to be the best of these steels, and after the use of sodium pyrophosphate and phosphoric acid as stabilisers was introduced, it was found that concentration at 60°C and then at 70°C could be carried out. Concentrations of 60% and later 80% and 90% were obtained in the laboratory.

During the same period Koroseal and other polyvinyl chloride resins appeared on the market. These were found to be suitable materials for gaskets, tubing, etc. and with these two new materials Electrochemische Werke was ready to consider large scale manufacture.

In 1934, Dr. Walter of the Walter Werke A.G. Kiel came to Dr. Pietsch with a request for 50% H_2O_2 in order to work out some ideas on power generation in military devices. Pietsch offered to develop a supply of 80% material which was better than 50% for the purpose intended. Walter had a small diesel engine plant along the Kiel Canal and appears to have been an obscure engineer. Pietsch was impressed with the idea of using strong H_2O_2 for power generation and proceeded to back up Walter vigorously. He became the prime mover in pushing the developments. He and his associates in the Electrochemische Werke, Adolph and Merck, advanced 400,000 RM for this work.

The first developments were on the decomposition of H_2O_2 by a catalyst to form superheated steam and oxygen, which were used to drive a turbine. This was followed by the use of fuels with H_2O_2 . Jets for Rockets were later developed and then jets for auxiliary starting devices for airplanes were developed and adopted. This was followed by submarine turbines and then by propulsion for torpedoes. A 500 H.P. torpedo was eventually developed with a speed of 50 miles per hour and a range of 15 miles, travelling without producing gas bubbles. Submarine engines of 2,000 H.P. and then 5,000 H.P. were developed and 6 boats built with two 5,000 H.P. engines each, which could travel about 30 miles under water without discharging air bubbles. These were never put into service because of the bombing of Kiel. About 1935 the German Navy became interested and in 1936 the Luftwaffe. Admiral Doenitz, when he became chief, pushed these developments aggressively but Admiral Raeder was never interested to the same extent. The Navy advanced 10,000,000 RM. for the construction of an experimental plant at Kiel, which sum was later increased by another 10,000,00 RM. Pietsch

claims that his part was strictly chemical and that he was not well acquainted with the mechanical details of these developments, so that his information is of a general nature only. Walter was captured by the British after the fall of Kiel. The principal chemical difficulty encountered was to obtain complete decomposition of the H_2O_2 , as explosions took place when liquid H_2O_2 came into contact with fuels. This was solved by producing H_2O_2 of higher purity which did not poison the decomposition catalyst.

By January 1939, progress had reached the point where construction of the Bad Lauterberg plant, with a projected capacity of 1,200 tons per month, 80% H_2O_2 was justified. Construction at Rhumspringe with a projected capacity of 2,100 tons per month 80% H_2O_2 was started in April, 1943. Somewhat later an underground plant of greater capacity was considered but never carried very far because bombing of the Krupp plant cut off the supply of stainless steels and the shortage of platinum became acute. The Government's objective was a production of 6,000 tons per month 80%, or about 8 times the world production on the same basis.

An interesting development was the direct synthesis by an electric discharge process carried out by Electro-Chemische Werke. The platinum shortage stimulated the search for non-electrolytic methods of H_2O_2 production as a result of which the 2-ethyl anthraquinone method worked out by I.G. was developed. This is based on the alternate reduction of 2-ethylanthraquinone to 2-ethylanthranol by hydrogen, followed by oxidation of the 2-ethylanthranol with 40% O_2 to 2-ethylanthraquinone and H_2O_2 in 50-50 solution of benzol and hexanol or $C_7 - C_{11}$ alcohols. The H_2O_2 is extracted by water from the organic medium in a special tower. The 20% peroxide solution so produced contains benzol, alcohols, and some water soluble acids. The output of a 5-ton per day pilot plant, when sent to Electrochemische Werke for concentration to 80% caused a great deal of trouble and loss and was considered dangerous to handle. A process of purification by dialysis was later worked out by I.G., but the Ludwigshafen pilot plant blew up before all the troubles were straightened out. I.G. was commissioned to build a large plant at Heydebrecht in Silesia for the production of dilute H_2O_2 by this process. Electrochemische Werke was ordered to disclose its process of concentration to I.G. so that it could be installed at Heydebrecht. The plant was started but not completed before the end of the war.

PROPERTIES OF HYDROGEN PEROXIDE 80 - 85%

Known as T Stoff it is almost a colourless liquid of specific gravity 1.35. It is corrosive and care must be taken to avoid contact with clothing, wood or oil or with the skin. If T Stoff does begin to heat up or decompose then it should be cooled by spraying water on the container or dilute it with water. The products of decomposition are 62% superheated steam and 37.6% oxygen at a temperature of 505°C.

Decomposition of T. Stoff under proper storage should be extremely slow but it must be protected from direct heat, radiation and from dirt.

For personnel handling T. Stoff a P.V.C. weave clothing has been manufactured to protect from splashes. Glasses and rubber gloves should be worn when pouring from containers. Splashes of peroxide on the skin are not serious if washed off within 15 seconds but if in contact for a longer period a second or third degree burn will result.

CATALYST.

The T Stoff is decomposed by numerous forms of catalyst. Nearly all the catalysts are compounded with manganese dioxide, the liquid catalysts which are not so convenient in use are sodium and calcium permanganates known by the code name of Z Stoff. The basis of most solid catalysts is a porous stone which will absorb the catalyst salts and this stone is impregnated with liquid catalysts.

FUEL.

Various fuels are used with Hydrogen Peroxide to combine with the oxygen released by its decomposition. In the case of the Rocket motor the fuel is a mixture of Hydrazine Hydrate, Methyl Alcohol and water known as C Stoff. In all cases it is important to use a sulphur free fuel.

GERMAN CAPACITY FOR HYDROGEN PEROXIDE

The following is a note of the German capacity for 35% Hydrogen Peroxide and 80% Hydrogen Peroxide during the 1939-1945 War.

Company	Location	Process	Capacity Tons/Mth as 35% H ₂ O ₂	Capacity Tons/Mth as 80-85% H ₂ O ₂
Kali Chemie	Honningen	BaO ₂ Barium Peroxide Process	120-150	-
Oesterreichischer Chem. Werke	Weissen- stein	H ₂ S ₂ O ₈ Persulphuric Acid Weissenstein Process	200	-
Degussa	Rheinfelden	ditto	400 (200 additional being built)	-
Riedel de Haen	Kufstein	(NH ₄) ₂ S ₂ O ₈ Ammonium Persulphate All liquid Process Loewenstein Process	200	15
Henkel & Co.	Dusseldorf	K ₂ S ₂ O ₈ Potassium Persulphate Precipitation Process Pietsch & Wolf also (NH ₄) ₂ S ₂ O ₈ Schmidt Process	160-180	-
Electro Chem. Werke, München	Hollriegel- skreuth	K ₂ S ₂ O ₈ Potassium Persulphate Precipitation Process Pietsch & Wolf	535(a)	500 (b)
(c) Otto Schickert & Co. (A branch of the Electro. Chem. Werke, München)	Bad Lauter- berg	ditto	3,500	1,200
Otto Schickert & Co.	Rhumspringe	(d) ditto. Never in production	2,000 nearly ready but not worked (4,000 extra planned)	2,100

Total Production 5115 - 5165 tons 35% H_2O_2 per month

Hydrogen Peroxide Requirements for
Commercial Production .

= 500 tons 35% H_2O_2
per month

Total Planned Production 11,000 tons + 4,250
by the Ethyl Anthraquinone Process

= 15,250 tons 35% H_2O_2
per month

World's Production

= 2,000 tons 35% H_2O_2
per month

(a) The original 35% H_2O_2 plant destroyed by bombing in July 1944.
New plant almost ready to operate April 1945 - Capacity 140 tons.

(b) Cost of Concentration plant was:-

	RM.	
Equipment	245,000	
Buildings	<u>100,000</u>	
	345,000	exclusive of utilities and other general plant facilities.

Apart from Lauterberg all the other Hydrogen Peroxide producers in the Greater Reich sent their 30 - 35% H_2O_2 to Hollriegelskreuth for purification and concentration with the exception of Kufstein Factory.

(c) 5 Units. Construction started January 1939. One unit completed January 1941. 5th Unit completed December 1944. Cost of construction 70,000,000 RM. and the Air Ministry supplied the Funds. Normal cost considered to be 45,000,000 RM. Cost of concentration unit 3,000,000 RM.

(d) 3 Units. Construction started April 1943. 1st Unit 80% completed in April 1945. 3rd Unit scheduled for completion March 1946. The Rhumspringe plant was expected to cost 120,000,000 RM.

NAMES UNDER WHICH CONCENTRATED HYDROGEN PEROXIDE WAS KNOWN.

Concentrated Hydrogen Peroxide was known under various code names such as T Stoff, Subsidol, Aurol, Ingolin, Geprol, Renal, Thymol, Oxylin, Neutralin and Ferhydrol. The last two names generally refer to 35%.

GRADES OF CONCENTRATED HYDROGEN PEROXIDE.

Concentrated Hydrogen Peroxide is classified into three grades - TN, TS and TSS.

TN = T Normal was the original production, signifying normal quality. It was somewhat impure and was stabilised with 0.3 g. $\text{Na}_4\text{P}_2\text{O}_7$ per litre and 0.3 g. hydroxyquinoline per litre. It was specified as 80 per cent strength and was discontinued.

TS = T Stoff Stabilisiert, the main product at Hollriegelskreuth, for Land Army, was very pure. It was stabilised with 0.02 g. H_3PO_4 per litre and no other stabilisers. It was originally 85 per cent but later 82 per cent strength. E.W.M. proposed TS as a general standard.

TSS = T Stoff Special Stabilisiert was made at Bad Lauterberg as a super stabilised quality for torpedoes (T.S. is satisfactory for submarine use where P.V.C. bags are used cooled by the sea water, but not for torpedoes), because the acceptance specification provides for storage at 50°C. for 9 months to cover tropical use. It was stabilised with 0.3 g. $\text{Na}_4\text{P}_2\text{O}_7$ per litre, and 0.3 g. 8-hydroxyquinoline per litre and was 85 per cent strength. Phosphoric acid was also added, 0.15 g/lt.

PROCESSES USED IN GERMANY.

The processes used in Germany are as follows:-

(1) Barium Peroxide Process.

In Germany the old barium peroxide process is still worked by Kali-Chemie at Honningen, and by Chemische Fabrik, Coswig-Anhalt.

(2) Persulphuric Acid. Weissenstein Process.

This process is worked at Weissenstein, Austria by the Oesterreichischer Chemische Werke and by licence at Rheinfelden by Degussa.

Production started at Weissenstein in 1908 and at Rheinfelden some twenty years later.

Sulphuric acid is electrolysed to persulphuric acid which is distilled to give 35% hydrogen peroxide leaving sulphuric acid for return to the electrolysis stage. During each cycle part of the sulphuric acid is purified by distillation.

(3) Potassium Persulphate Precipitation Process - Pietsch & Adolph.

Plants for this process are sited in Germany at Bad Lauterberg, Rhumspringe, Munich and Dusseldorf. At the first three places the peroxide can be concentrated up to 85% strength.

Ammonium bisulphate solution is electrolysed to give ammonium persulphate in solution.

Potassium bisulphate is added to this solution to precipitate potassium persulphate and to leave a solution of ammonium bisulphate which is returned to the electrolytic cells after purification.

The potassium persulphate is treated with sulphuric acid and steam distilled to give hydrogen peroxide vapour which is fractionated to 35% strength.

The residue of potassium bisulphate and sulphuric acid is crystallized to give potassium bisulphate solid, for return to the precipitation stage, and sulphuric acid solution for re-use in the distillation stage. This sulphuric acid has to be purified before returning to the stills.

The 35% hydrogen peroxide is then distilled and concentrated to yield the 80/85% hydrogen peroxide.

(4) Ammonium Persulphate Process.

(a) Loewenstein Process (Kufstein)

This process is worked by Elchemie, a company formed by Schering and Riedel de Haen at Kufstein.

Hydrogen Peroxide of 30% strength is produced by a completely liquid process from the distillation of an ammonium persulphate solution, which has been prepared by the electrolysis of ammonium bisulphate. There is a purification stage for the liquor between the distillation and electrolysis.

Hydrogen Peroxide of strengths up to 90% is produced in a climbing film evaporator of an elaborate design such that 26 - 30% hydrogen peroxide is distilled in one set of evaporators, and the purified distillate is concentrated in another set. Only two out of the eight stills at Kufstein have been converted in this way to produce the high strength hydrogen peroxide.

The process (up to the 30% strength) was worked out at Berlin Britz by the firm of Riedel de Haen in 1929, and the Kufstein plant was built in 1931. The plant is somewhat primitive and has not been improved since its installation.

(b) Schmidt Process

There is a unit of this at Henkel's Duneberg Factory.

The Henkel original electrolysis unit was on a small scale but later a much larger bath had been developed and the results appeared promising.

(5) Anthraquinone Process.

Dr. Georg Pfeleiderer had worked out this process at the I.G. Works, Oppau, Ludwigshafen and a pilot plant was worked there capable of producing 5 tons 20% hydrogen peroxide per day. This pilot plant has been shipped to the United States in the charge of the U.S. Naval Technical Mission in Europe.

Ethyl anthra-quinone is reduced by hydrogen in the presence of nickel catalyst to give quinhydrone. The quinhydrone is then oxidised to reform the quinone with the formation of hydrogen peroxide. These two operations are carried out in an organic solvent solution from which the hydrogen peroxide is finally extracted by water.

Two very large plants were being built by the German Government, at Heidebreck and Waldenberg, both in the Russian zone. The reason given for the adoption of the process was the shortage of platinum which precluded the further extension of electrolytic processes. However, the view was generally expressed by the peroxide experts in Germany that the process was an undesirable one. There is an explosive risk in working the process, one explosion having killed all the men working on the pilot plant. For the high strength hydrogen peroxide it appears that they have not been able to produce an aqueous solution of hydrogen peroxide sufficiently free from organic matter.

(6) Direct Synthesis by Electric Discharge

Dr. Krutzsch of Electro-Chemische Werke, Munich has been working on this process for 14 years.

Hydrogen with 5% oxygen and saturated with water vapour is passed between parallel quartz plates which have been coated with aluminium on the outer side. High voltage, high frequency electric discharge is applied to the plates resulting in the combination of the hydrogen and oxygen to give a mixture of water and hydrogen peroxide. The gases are circulated through the plates, a heat exchanger and scrubbing tower, the hydrogen peroxide being obtained from the tower.

Experiments were carried out first in a one Kw. and then in a 10 Kw. unit. A 100 Kw. unit was being built but was bombed before completion. Plans had been prepared for a 200 Kw. plant to produce 30 Kg. 100% hydrogen peroxide per hour, but the opinion was expressed by the Germans that the process had not reached the stage of being able to compete with the persulphate. It is higher in consumption of electricity, but would have an advantage as far as labour is concerned.

A practical figure obtained by Krutzsch for electricity was:

62.6 KWH per Kg. hydrogen peroxide 100%

This figure includes electricity for the production of the hydrogen and oxygen and for power.

Other methods of direct synthesis are being investigated throughout the world but it is not considered that they have advanced sufficiently far to influence the present decision for fulfilling immediate requirements.

BAD LAUTERBERG

This factory in the Hartz, output 1200 tons per month H_2O_2 80%, was constructed by the firm of Otto Schickert & Co. an affiliated company of the Electrochemische Werke, Munich, formed in November 1938.

Management.

President	Otto Schickert - General Management
Vice President	Dr. Ing. Werner Piening - Technical Department
				Dr. Phil. Wilhelm Reggelin - Chemical Department
				Dipl. Ing. Wolfgang Schubert - Designing & Construction.
				Dr. Heinrich Glaeser - Manager of Laboratory.

All these members of the Management were interviewed and Dr. Piening and Dr. Reggelin accompanied us round the works.

Chemical Process.

The chemical process adopted at Bad Lauterberg was that which was developed by Pietsch and Adolph at the Electrochemische Werke, Hollriegelskreuth, München. The operations are divided into four:-

- (a) Electrolysis of ammonium bisulphate to form ammonium persulphate solution.
- (b) Conversion of ammonium persulphate to potassium persulphate crystals by reaction with potassium bisulphate, with regeneration of the ammonium bisulphate.
- (c) Hydrolysis of the potassium persulphate with live steam and rectification of the resultant H_2O_2 - H_2O vapours to produce 35% H_2O_2 , with regeneration and purification of the potassium bisulphate.
- (d) Concentration of the 35% H_2O_2 solution to 80 - 86% by vaporisation and rectification under vacuum in special equipment.

Overall Requirements.

The overall requirements of raw materials, power, etc. per 100 kg. of 100% H_2O_2 are:-

1521 KWH AC electric power for electrolysis
 224 KWH AC electric power for other purposes
 15 Kg. 100% H_2SO_4 divided about

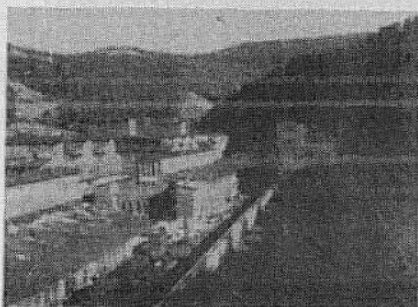
55% contact acid
 45% from SO_2 added to the H_2SO_4 prior
 to purification to eliminate H_2O_2 .

1.75 Kg. K_2SO_4
 3.8 kg. NH_3
 0.96 kg. NH_4CNS added to the electrolyte at the rate
 of 0.1 gram/litre to increase oxidation tension.
 0.14 gram platinum net loss

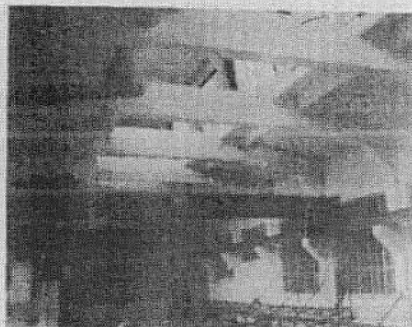
Gross Loss	0.20 gram
Recovery	<u>0.06 gram</u>
Net Loss	0.14 gram

0.17 kg. $K_4Fe(CN)_6$
 2.8 tons steam
 25 man hours

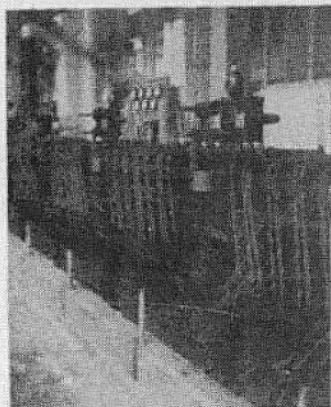
BAD LAUTERBERG



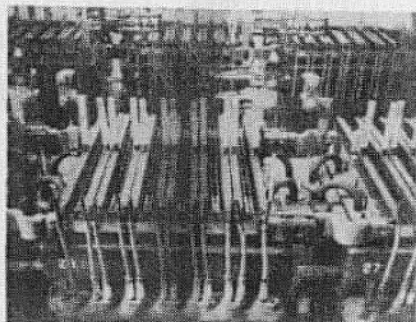
View from Boiler House
Roof.



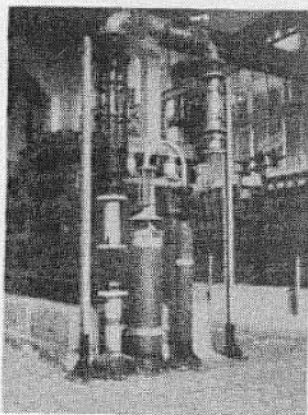
Internal Construction of
Hall - Centre Span.



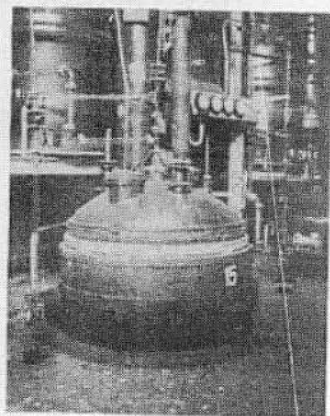
Battery of Cells.



Arrangement of Cell.

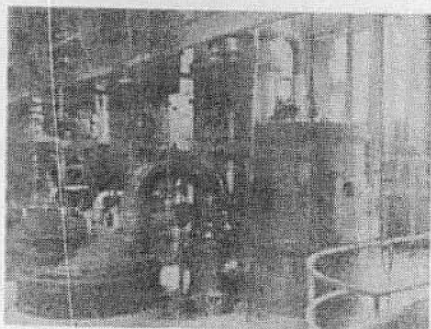


Cell showing Feed
arrangements.

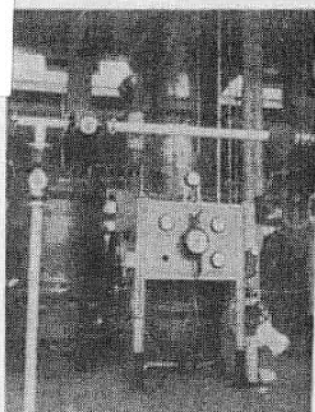


Concentration Plant.

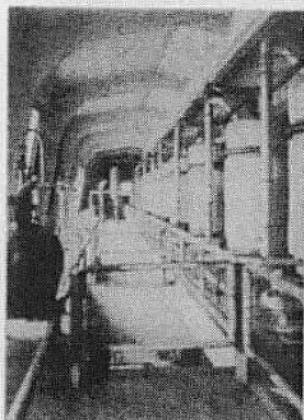
BAD LAUTERBERG.



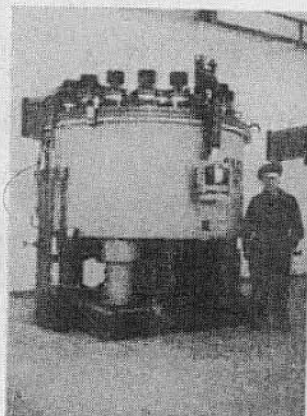
Distillation Plant



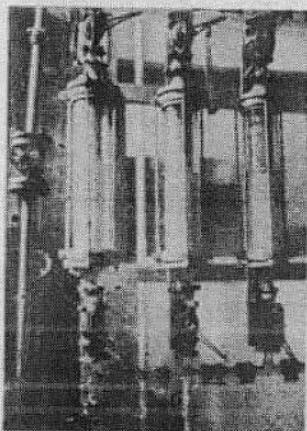
Concentration Plant Control.



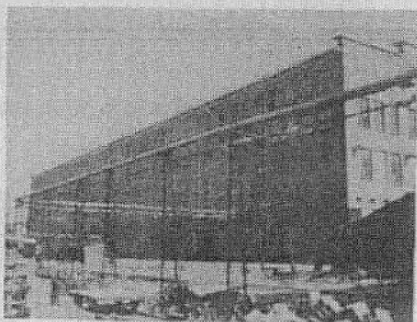
Condenser Line
above Stills



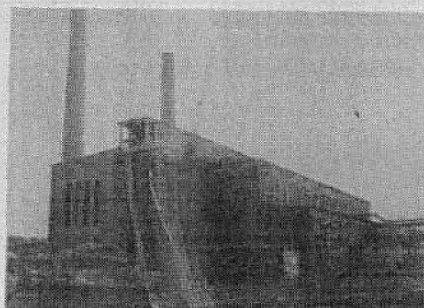
Mercury Arc Rectifier



Peroxide Filters.



Hall under Construction.



Main Boiler House.



Arrangement of Cell
Batteries.