ASSESSMENT AND MINIMIZATION OF MERCURY LOSSES IN A MERCURY CELL BASED CHLOR – ALKALI PLANT

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DOCTOR OF PHILOSOPHY

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CERTIFICATE

This is to certify that the thesis entitled "Assessment and Minimization of Mercury Losses in a Mercury Cell Based Chlor-Alkali Plant" submitted by Mr. Ranveer S. Mahwar, ID No. 76S83003, for the award of Ph.D. degree of the Institute embodies original work done by him under my supervision.

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ABSTRACT

In a chlor-alkali plant using mercury cell process, 87.9% mercury is lost in brine sludge, 5.2% in hydrogen and hydrochloric acid gases, 3.8% in cell cleaning waste water and 3.1% in other miscelleneous forms. Chlorination of the sludge converts insoluble mercury to soluble form and the filterate can be recycled to brine electrolysis cells. For 1 kg of sludge a chlorine flow of 0.62 gms/minute for 5 minutes and an additional 50 minutes of agitation converts 83.9% of the insoluble mercury in sludge to soluble forms. About 95% of this soluble mercury can be extracted by filteration and washing of the chlorinated sludge to give an over all 80% recovery. Cell cleaning waste water was found suitable for recycle to brine system. This recycle should be limited to first 30 minutes of the cleaning operation, as most of the mercury losses are detectable in this time. From hydrogen gas, mercury can be recovered by adsorption on activated carbon. A grain size 4/16 mesh for activated carbon, L/D ratio of 2.4 for adsorption bed and flow rate of 26.8 litre/hr (for 100 gms of carbon) of feed stream was found optimum. The adsorption capacity of the carbon under these conditions was found to be 0.374 gms of Hg/Kg of the activated carbon. Due to the shallow shape of the 'Break through curve' a three stage cascade system involving two bed in series for adsorption while the third is in regeneration was found suitable for this purpose. Regeneration of the bed can be done by passing hot air (with flow equivalent to 181.7 litres /hr at STP) to maintain a bed temperature of 100°C.

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INTRODUCTION

1. INTRODUCTION

1.1. Mercury and Its release into Environment:

Mercury is an important substance for man because of its wide variety of applications in industry, medicine and agriculture. It is of interest to note however, that inspite of its innumerable application, this material could draw much attention of the world only after the incident of mercury poisoning in Japan, the famous "Minamata" desease in sixties. This made man alert and he started studying its ill effects and minimization of its release into the environment.

Mercury is released into environment both by natural as well as anthropogenic means. The major natural source is the degassing of earth crust which amounts to about 25,000 - 1,25,000 tonnes per year[1]. Anthropogenic sources can be grouped in two broad categories, (i) Direct sources and (ii) Indirect sources.

Direct sources include those industries which use mercury in their manufacturing processes and are responsible for its subsequent release into environment. Important among these are chlor-alkali, electrical equipments, paints, measurement and control systems and pharmaceuticals. Besides these, mercury also finds application in agriculture and dental purposes. Regarding the total quantity released through direct sources, it is interesting to note that according to Korringa and Hagel[1] all the 10,000 tonnes mercury produced per year by mining and smelting find its way back into environment.

Indirect sources are those activities of men which are not directly related to mercury. These include burning of fossil fuels, production of steel, cement and phosphate and smelting of metals from their ores. The total estimated release of mercury in these is 10,000 tonnes per year[1]. This means that the quantities released by direct sources as well as indirect are of the same order of magnitude.

1.2 Need for the control of Mercury Losses from Chlor-Alkali Industry:

Control of Mercury losses is important because of following two reasons :

(i) Mercury is an expensive material and therefore its loss/is likely to disturb the economic equilibrium of the industry, and

(ii) Unlike natural sources, its release from industries can give rise to untolerable localised concentrations leading to damages to life.

Among mercury using industries, chlor-alkali industries are estimated to release about 25 percent of the total mercury released into environment from direct sources[1]. This industry, therefore, should be given priority in reference to this problem. For India, the importance is further enhanced due to following considerations :

1. Mercury is an imported material and about 50 percent of the total 265 tonnes annually imported is consumed by chlor-alkali industry alone[2].
2. Many of the rivers which receive mercury contaminated waste water discharged by the industries are seasonal. This further adds to the severety of this problem because of the inadequate dilution in the receiving stream.

1.3 Mercury and Chlor-Alkali Industry :

1.3.1 Mercury Cell Process for Caustic Soda Manufacture:

Out of the two processes widely used for caustic soda manufacture namely - (i) Diaphragm Cell Process and (ii) Mercury Cell Process: the latter is preferred because in this process a caustic liquor containing upto 73 percent NaOH of unusually pure quality can be made. This is in contrast to the diaphragm cell process which gives a caustic liquor containing 10 to 13 percent NaOH and an equivalent amount of undecomposed salt[3]. In our country about 80 to 85 percent of the caustic soda is produced by Mercury cell process.

The principle and important steps of the process can be understood by block diagram shown in Fig.1.1. Brine of required concentration and quality is prepared and continuously fed to electrolysis cells. These cells, commonly known as "primary cells" consist of mercury as flowing cathode and graphite as anode. Sodium amalgam is formed and chlorine gas is liberated as a by product :

$$NaCl + x\,Hg \rightarrow NaHg_x + \frac{1}{2}\,Cl_2$$

Sodium amalgam thus formed then enters into decomposers where it reacts with water to give sodium hydroxide and byproduct hydrogen gas.

$$NaHg_x + H_2O \rightarrow NaOH + 1/2\,H_2 + x\,Hg$$

Regenerated mercury from decomposers is recycled to primary cells. The depleted brine from primary cells is resaturated with salt and purified by treatment with suitable chemicals to make it suitable for electrolysis.

Depending upon need, chlorine is converted into liquid chlorine or burnt with hydrogen to make hydrochloric acid.

A detailed flow sheet of a chlor-alkali plant is shown in Fig. 1.2. For convenience the plant can be divided into following five sections.

(i) Cell House:

This is the main section of the plant where electrolysis of brine is done. The by-products hydrogen and chlorine are sent to other sections. Depleted brine from primary cells goes to brine house for resatuaration and purification.

(ii) Brine House:

Depleted brine, after dechlorination by bringing vacuum, goes to saturator where fresh salt is added. This resaturated brine then goes to purifiers where it is treated with suitable chemicals to precipitate impurities which come from the salt. The treated brine is then sent to a settler where most of the precipitated impurities are removed by sedimentation. Over flow from settler is filtered to remove residual suspensions. The filtered brine thus obtained is sent for electrolysis.

Sludge from settler is periodically drained into sludge pits where it is further allowed to settle. The decantated brine from these pits is recycled to purifiers. The bottom sludge, still containing significant quantity of brine, is filtered with the help of a rotatory drum vacuum-filter. Recovered brine is again sent to purifiers. The residue resulting from this filteration commonly known as drum filter cake, is disposed as a solid waste.

(iii) Hydrogen and Hydrochloric acid section :

Hydrogen gas from decomposers, after a two stage cooling, is burnt with chlorine in a furnace to give hydrochloric acid gas. This HCl gas is cooled in an absorber cooler and sent to an absorption tower where it is absorbed in water to give dilute hydrochloric acid. The later flows back into absorber-cooler where it further picks up HCl gas to give concentrated hydrochloric acid. The concentrated acid thus formed is continuously removed and sent to HCl storage tanks. Residual gases from absorption tower are scrubbed with water, which is then disposed as a liquid waste. Washed gases from scrubber are vented to atmoshpere.

(iv) Chlorine section:

Chlorine gas liberated in primary cells is cooled and, after mist elimination, is partly converted in liquid chlorine and rest is used for making hydrochloric acid. For maintaining a constant pressure a water seal is provided before cooling etc. Waste water from this seal is continuously discharged.

(v) Caustic Soda Section:

Product caustic soda from decomposers is cooled, filtered and sent to storage tanks.

1.3.2 Origin and control of mercury losses:

Since mercury is present in the primary cells and decomposers, therefore out going streams from these i.e. caustic soda, Hydrogen, Chlorine and depleted brine carry some mercury with them and therefore result in some mercury losses. Besides these some human negligence in handling mercury or related equipments can also give rise to mercury loss.

A systematic study is therefore essential to first identify all mercury loss points and then to develop control strategies. This will require analysis of various air, water and solid matters which are likely to contain mercury and then studying various alternatives for controlling mercury.

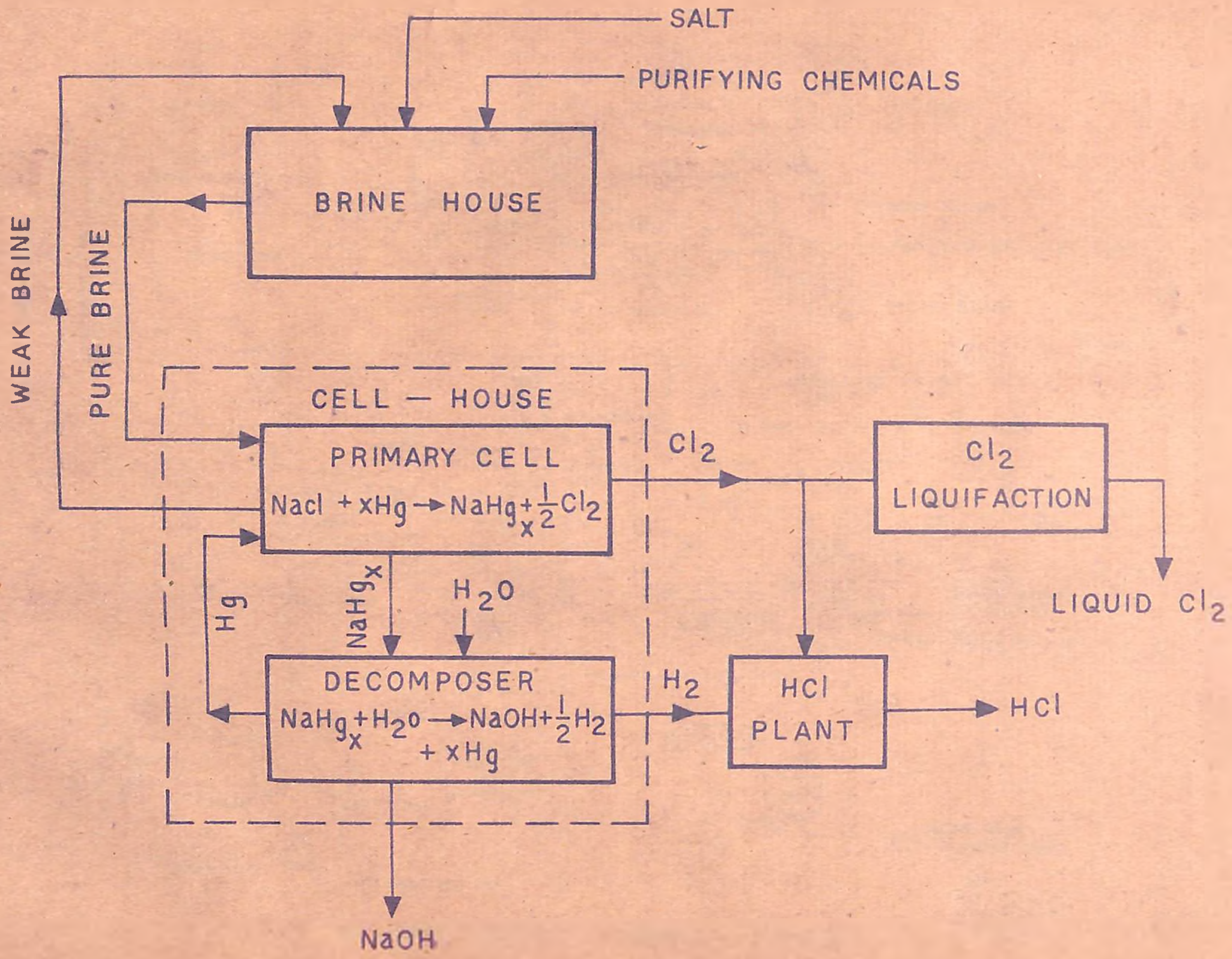


FIG. 1.1 Caustic Soda Production by Mercury Cell Process.

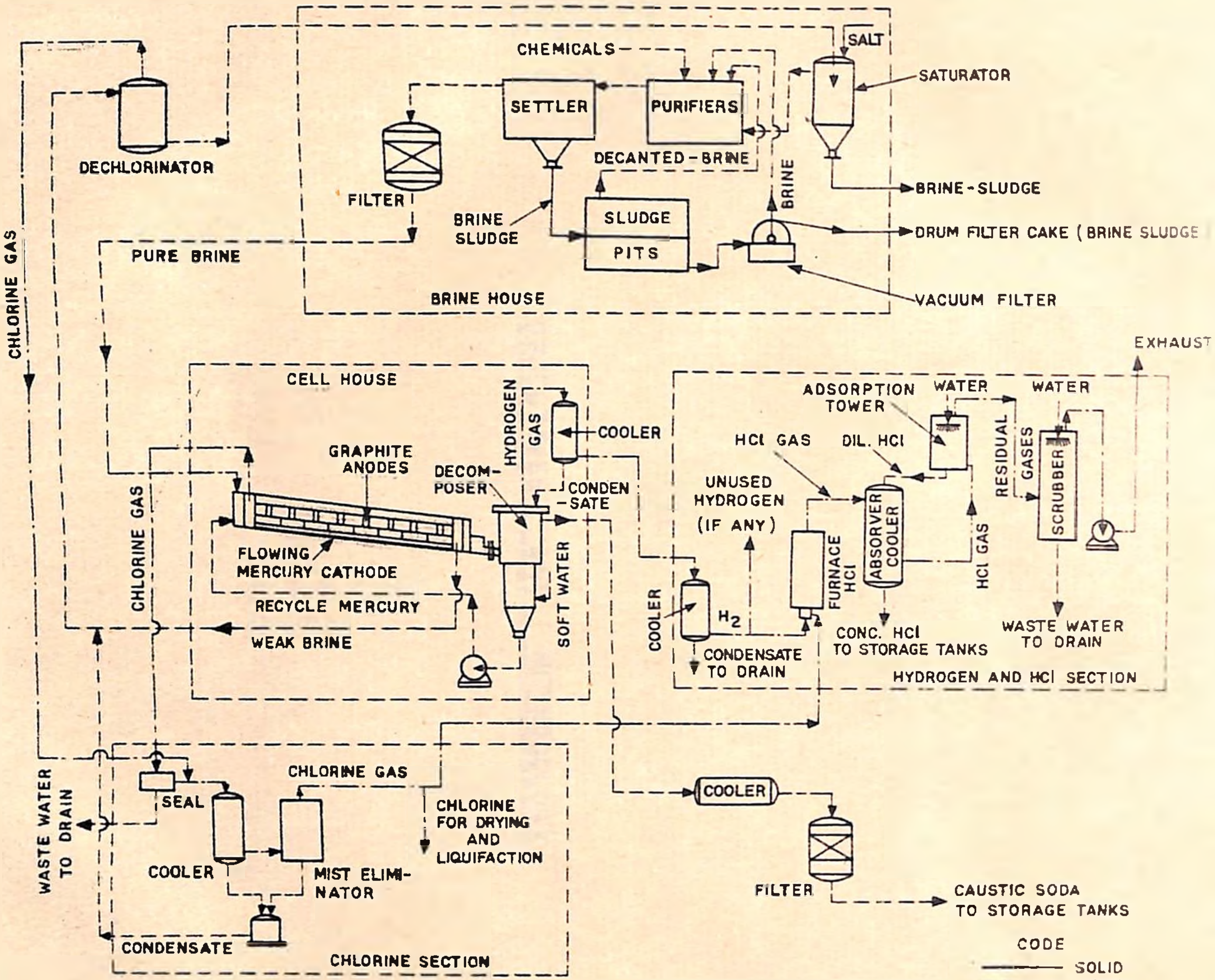


FIG. 1.2 Flow Sheet of a Mercury Cell Based Chlor-Alkali Plant.

OBJECTIVES AND METHODOLOGY

2. OBJECTIVES AND METHODOLOGY

2.1 The objectives of this study were :

(1) To identify mercury loss points in a mercury cell based chlor-alkali plant.

(2) To estimate mercury losses from various loss points and thereby identify major loss points.

(3) To make a comparative study of various alternative methods for mercury control and thereby identify most suitable and plausable technique(s).

(4) To make further studies on already identified (in objective 3) control techniques for optimizing various parameters.

(5) To suggest a comprehensive scheme for minimizing mercury losses from a mercury cell based chlor-alkali plant.

This study was conducted in a real life situation. All the experiments were performed in a Mercury Cell based chlor-alkali plant which produces over 100 Tons/day of caustic soda.

2.2. Methodology:

This entire research work has been done keeping problem solving approach in mind. Although, according to statistics, the plant has very low mercury loss compared to the average mercury loss in Indian chlor-alkali plant , the plant management is conscious about the mercury loss both because of its effect on environment and foreign exchange drain. A systematic and scientific detailed study was therefore planned in consultation with plant personnel. Continuous contacts were maintained with the host organization's experts for their valuable suggestions. The methodology is outlined below.

First all the possible points of mercury loss were identified in all air, liquid streams and solid wastes. Their samples were then analysed for mercury content (using ISI prescribed technique) and corresponding quantity was also estimated. This provided the total mercury loss which was compared with the plant inventory data. This process was continued, and some new possible points were identified and analysed until a satisfactory check and balance was obtained. Knowing an exhaustive list of loss points and their contributions, major contributors were identified for further work in the direction of control of mercury losses.

An extensive literature search was made to find out various techniques available for mercury control from chlor-alkali industries. It was observed that techniques outlined in literature are not of general nature but most of them do not take into account the variation in operational and other conditions from plant to plant.

Therefore the major task then was to identify and select the technique(s) which are practical and suitable to the host organization for all air, water and solid wastes. Experiments were designed keeping the conditions of the plant in mind. Wherever possible control techniques providing opportunities for recovery and/or recycle of mercury were preferred for obvious reasons. After selections of suitable technique(s) for air, water and solid wastes detailed experiments on each were then conducted in laboratory for optimizing important parameters. A comprehensive scheme for the total was then recommended identifying techniques and optimum conditions. It should be mentioned here that no attempt has been made for designing the equipments involved in suggested techniques as it was not within the objectives of this study. However, values for important variables required for design work have been identified. The designing aspects of the suggested scheme have been left to the design group of the host organization. It will also be important to mention here that a part of the scheme (discussed in chapter VII) has already been implemented by the host organization and is working satisfactorily.

LITERATURE SURVEY

3. LITERATURE SURVEY

Literature was reviewed for identifying a suitable method of the analysis of mercury and also for various available techniques for removal and or recovery of mercury from chlor-alkali industries.

3.1 Mercury Analysis :

Atomic absorption, neutron activation and colorimetric analysis (dithizone) have been reported as the most frequently used methods for the measurement of total mercury.

3.1.1 Atomic Absorption Analysis :

The procedure involves conversion of mercury present in a sample into gas phase and measurement of mercury vapor absorption at 253.7 nm wavelength. A long series of variants of this principle has been used for the analysis of mercury in biological samples. The essential difference between various methods is the way in which mercury in the sample is converted into mercury vapor. The detection limit has been reported to be approximately 1-5 ng of mercury[1].

3.1.2 Neutron Activation Analysis :

This method is based on the principle that when natural mercury is exposed to a high flux of thermal neutrons, it is converted to a mixture of radioactive isotopes 197 Hg and 203 Hg, which have decay half lives of

65 hrs. and 47 days respectively. For analysis, samples are sealed in quartz tubes and subjected to neutron irradiation. Mercury concentration is then measured by the direct gamma - spectrometric determination of the 197 Hg formed in relation to a known standard. The limit of detection is reported as 0.1 - 0.3 ng of mercury[1].

3.1.3 Colorimetric Analysis:

This method involves wet digestion of the sample with oxidizing acid solutions and extraction with complexforming substances (mainly dithizone) in an organic solvent, followed by colorimetric determination of mercury complex. Detection limit has been reported to be 0.05 μg of mercury in air samples and 0.5 μg in other samples[1].

3.2 Removal/Recovery of Mercury: from chlor-alkali industry:

Techniques reported for removal and or recovery of mercury from a chlor-alkali plant can be grouped into the following three classes:

(i) From solid wastes

(ii) From liquid streams, and

(iii) From gases.

A summary of important and relevant information found is given below:

3.2.1 Recovery/Removal from solid wastes:

The major solid waste is the brine sludge. Two methods have been suggested for mercury recovery (i) chemical oxidation and (ii) Roasting.

3.2.1.1 CHEMICAL OXIDATION :

This involves treatment of sludge with chlorine or compounds containing active chlorine such as sodium hypochlorite. This converts insoluble mercury to soluble mercuric ion. The mercuric ion thus formed gives a highly soluble tetra chloro complex in the presence of chloride ions. This treated sludge is filtered to separate soluble mercury and the filterate obtained can be recycled to the electrolysis cells if it meets the quality.

Sodium hypochlorite has been widely used in Japan and United States. Osaka Soda Ltd. of Japan claims a reduction in mercury concentration from 50 to 400 mg/kg (dry basis) in brine sludge to 0.1 mg/kg.[4]. Use of sodium hydroxide and chlorine (which react together to give sodium hypochlorite) has been suggested by FMC Corp. of USA[5].

Addition of chlorine gas (chlorination) to the sludge to dissolve mercury has also been reported. It has been mentioned that 70-90 percent of the insoluble mercury present in the sludge can be converted to soluble form by this treatment[6]. In an alternative method oxidant chlorine is directly generated in situ by the electrolysis of sodium chloride present in the sludge[6]. The method however, has not been significantly successful than the direct addition of chemicals.

3.2.1.2 Roasting :

In this technique the sludge is heated to evaporate mercury. The emerging gases are then cooled to condense mercury. This method has been successfully tried by Georgia Pacific Corporation of USA. Upto 99.8 percent mercury removal has been claimed by using a gas fired multiple hearth furnace for heating the sludge at about 750 - 760° C[5,6].

3.2.2 Recovery/Removal from Liquid Streams:

Liquid streams likely to contain mercury in the plant are waste water from various sections such as cell cleaning water from cell house, waste water from hydrochloric acid plant etc. Suggested methods are reduction, Ion-Exchange, Sulfide precipitation and Adsorption.

3.2.2.1 Reduction :

This involves reduction of the mercury ions present in waste water to metallic state followed by filteration. The residue consisting of crude mercury has to be further distilled to get pure mercury. Commonly reported reducing agents are sodium borohydride and metals such as zinc.

Vention corporation of USA which manufactures sodium borohydride, claims that their technique which uses this compound to precipitate mercury out of waste waters is capable of reducing mercury to very low levels[6,7]. For zinc, a 99 percent mercury removal using a dosage of 3.8 kg of zinc per kg. of mercury has been reported[6].

Out of the several chemicals suggested sodium borohydride has been reported to be more desirable as it is relatively inexpensive and also does not create any secondary pollution problem. For example use of zinc is likely to create zinc pollution problem.

3.2.2.2 Ion-Exchange:

In this technique mercuric ions present in waste waters are removed by using ion-exchange or chelating resin. This technique however, is generally preferred in cases where very stringent mercury pollution standards have to be met.

Akzo Zout Chemie of Netherland has developed a technique for reducing mercury concentration in waste waters using ion-exchange method. Their trade named 'Imac-TMR' resin has been reported to be a polymeric mercaptan in which thiol groups are attached to a microporous styrene / divinylbenzene copolymer[8].

Osaka soda Ltd. of Japan has also developed a technique which consists basically of two step ion-exchange, with different proprietary resins used in each step. The couple of resins has been given the trade name as 'IE-MR' resin and has been reported to be very efficient[9].

In both the above mentioned processes it is said that the regeneration of the resin and recovery of mercury is possible with suitable chemicals such as hydrochloric acid.

3.2.2.3 **Sulfide Precipitation:**

A number of publications have described the use of sulfide ions for precipitation of mercury from waste waters as mercury sulfide. An optimum pH of 8.5 has been reported for most effective precipitation[10]. Precipitation may possibly be combined with flocculation and separation by gravity, filteration etc. The residue containing mercury sulfide requires further treatments for mercury recovery.

FMC of USA has developed a technique using sulfide precipitation method and has been reported to be in operation in the firm's shlor-alkali plant in Squamish, British Columbia[5].

3.2.2.4 **Adsorption :**

In this technique waste water is passed through a bed of activated charcoal to adsorb mercury.

A process involving this principal has been developed by Bellingfors Bruks of Sweden. Their special adsorbent trade named as 'BMS adsorbent' has been reported to be activated charcoal, with a special surface preparation using sulfur compounds for selective adsorption of ionic mercury[9].

3.2.3 Recovery/Removal from Gases:

Hydrogen gas and chlorine gas liberated in the caustic soda production and cell house air are likely to contain mercury. However hydrogen being in contact with mercury in the process, carries a significant quantity mercury vapors and techniques reported to remove these vapors are (i) scrubbing and (ii) adsorption.

3.2.3.1 Scrubbing :

Hydrogen gas is scrubbed with chlorinated brine or sodium hypochlorite to remove mercury. Resulting scrubbings, containing dissolved mercury, can be recycled to brine system. Reduction of mercury concentration upto 0.8 mg/m^3 in hydrogen gas has been reported[11].

3.2.3.2 Adsorption:

Activated carbon as such or in combination with other compounds has been used to adsorb mercury from hydrogen gas.

Sobin chlor-alkali Co. of USA has been reported to be using an adsorbent called 'purasive mercury' from Union carbide, since 1972 and an efficient mercury removal has been claimed[11].

Another adsorbent process developed by Bayer, with an iodised activated carbon adsorber has been reported to be capable of reducing mercury in hydrogen to as low as 2 $\mu g/m^3$ [11].

3.3. Critical Assessment of Literature:

3.3.1 Mercury Analysis:

Out of the three methods available atomic absorption and neutron activation techniques are important when analysis of environmental samples, blood and food products etc., involving very low mercury levels, is required to be done. Dithizone colorimetric method on the other hand has been widely used for the type of work involved in the present study. This method is also recommended by Indian Standard Institution (ISI)[12]. The host organization has been using this technique successfully for quite sometime and it has been experienced that it has adequate sensitivity. It was therefore decided to use this method for the present study.

3.3.2 Mercury Recovery/Removal:

A review of the literature has clearly indicated that various scientific principles for mercury recovery / removal have been used by several chlor-alkali or technology selling industries to fit their needs. Also most of the techniques are patented and detailed information such as optimum parameters, process conditions etc.

are not reported. Moreover economic considerations will also vary from plant to plant and a technique which might be economically feasible for one plant might not be viable for the other. For example in case of solid wastes, roasting technique even with a very high efficiency, may not be economic for bigger plants generating large quantities of sludge with relatively lower mercury content. For a particular quantity of sludge (of known mercury) an approximate idea about the feasibility of this technique can be obtained by calculating the cost of fuel required to heat the sludge to desired temperatures . Like-wise use of chlorine or related compounds for this purpose may be economic for plants in India but may not be for plants in USA, because of a good market of chlorine in USA . This may also be true even for different plants in the same country . Therefore various oxidants should be tried and results should be compared to see their relative suitability for the given plant .

In case of liquid streams containing strong oxidants, mercury removal methods such as sulfide precipitation, reduction, ion exchange or adsorption may not be effective . This is because sulfides and any reducing agent used will be preferentially consumed by the oxidant . Oxidants are likely to damage the resin or adsorption bed. Moreover the quantity of mercury generally present in waste waters is quite small. It is therefore desired that whenever possible recycle of the waste water in the plant should be attempted.

Like liquid streams, losses of mercury in hydrogen gas are also not significant. However a different logic can apply here with respect to economics. The presence of mercury in this gas is likely to contaminate the hydrochloric acid produced from it. Hence, if mercury is removed from this gas and then used for making hydrochloric acid, the grade of this product may change from commercial to analytical which is of high price. This limits the choice of mercury removal from H_2 gas to adsorption technique only.

It is therefore clear from the above description that for any technique, whether it is for solid wastes, liquid stream or hydrogen gas, extensive experimental work is required to see its suitability and economic feasibility for a given plant. It should be mentioned here, that like any other pollution control, economic viability has different connotation. Economic feasibility does not necessarily mean that the total cost of the control technique should atleast balance the cost of mercury recovered. An attempt should be made to minimize the cost and maximize mercury removal and or recovery.

Based on the discussions given above, it is evident that for the removal and/or recovery of mercury from the chlor-alkali plant further work should be carried out in the following areas:

(i) Chemical oxidation and Roasting for solid wastes.

(ii) Possible recycling of liquid wastes.

(iii) Adsorption of mercury on activated carbon bed from Hydrogen gas.

THEORY

4. THEORY

Based on the information available in the literature and its assessment with respect to the present study, following conclusions were drawn in the previous chapter:

(i) Dithizone colorimetric method is to be used for the analysis of mercury.

(ii) Further work is needed for the chemical oxidation and roasting methods for mercury recovery/removal from solid wastes. For roasting feasibility should be first assessed for the concerned plant and if found viable experiments may be desired.

(iii) Possibilities of recycling liquid streams containing mercury to be explored.

(iv) Adsorption of mercury from hydrogen to be studied.

Some important theoretical concepts of these follows:

4.1 Dithizone colorimetric method of Mercury Analysis:

The principal of the colorimetric analysis is the 'Beer-Lambert Law', according to which light absorption by a sample is a measure of the concentration[13].

$$A = \epsilon c b$$

where -

A - Absorbance
ϵ - Molar extinction coefficient
c - Molar concentration of the solute in the sample solution
b - Thickness of the sample solution.

In the present case therefore absorption by the orange yellow complex formed by the reaction of mercury ion and dithizone (diphenyl thiocarbezone) is propertional to the concentration of mercury present. This reaction is carried out in acidic solution and the complex formed is mercuric dithizonate.

$$Hg^{+2} + 2\,C_{13}H_{12}N_4S \xrightarrow[\text{Medium}]{\text{Acidic}} Hg\left[C_{13}H_{11}N_4S\right]_2 + 2H^+$$

(Dithizone) (Mercuric dithizonate)

The complex formed is likely to contain excess of dithizone, which will interfere with colorimetric measurements. A correction is therefore required. Fig.4.1[14] shows that the complex and dithizone has maximum light absorption at 485 nm and 610 nm wavelengths respectively. Dithizone however also absorbs at 485 nm to some extent. For obtaining a correction, absorbance of the extracted complex is measured at both the 485 nm and 610 nm (measure of excess dithizone) and from a pre-obtained set of absorbance for dithizone alone at 485 nm and 610 nm absorption by excess dithizone present in complex at 485 nm can be obtained and necessary correction can be made. For example if A_{485} and A_{610} are absorbance values for the sample at 485 nm and 610 nm wave-lengths respectively and A'_{485} is the absorbance by excess of dithizone corresponding to A_{610} (obtained from above mentioned set of data for dithizone at 485 nm and 610 nm Wave-lengths). Then the absorbance by the mercury complex alone will be $(A_{485} - A'_{485})$.

Species which can interfear in this analysis are, metals such as copper, gold andsilver which form complexes with dithizone and oxidants such as Fe^{+3}, free halogens and permangnate which convert dithizone to a stable compound diphenyl thiocarbadiazone. These interferences can however be eliminated by masking the undesirable metals mentioned above with EDTA (ethylenediamine tetra acetic acid) and using hydroxylamine hydrochloride to avoid oxidation of dithizone. All the interfering metals mentioned above form stable complexes with EDTA and hydroxyl amine hydrochloride $(NH_2OH \cdot HCl)$ consumes the oxidants.

4.2. Mercury Recovery/Removal Techniques:

Before one understands theoretical principles involved for control techniques of mercury from various sources, it is desirable to discuss possible mechanisms and causes of mercury carry over in gaseous, liquid streams and solid wastes.

4.2.1 Mechanism of Mercury carry over:

As mentioned earlier, depleted brine, hydrogen gas, product caustic soda and chlorine gas are the modes of the transport of mercury from electrolysis system to various sections in the plant and are responsible for all the subsequent losses.

Presence of mercury in depleted brine is as a result of a reaction between chlorine contained in the brine and mercury (cathode) in primary cells forming soluble mercuric chloride. The later gets dissolved and carried by the dipleted brine leaving these cells. This dissolved mercury partly gets converted into insoluble forms during resaturation and purification of this brine and is carried in the sludge resulting from these operations. A relatively large quantity of mercury is expected to be carried by depleted brine and lost in sludge as a result of power failures. This is because of the fact that in normal running of the plant the conversion of mercury into soluble mercuric chloride described above in constantly opposed by the electrolysis effect which reconverts soluble mercury back into metallic mercury. The latter effect, however, disappers the moment power fails leading to increased concentration of mercury in depleted brine and hence loss in the sludge.

Hydrogen gas leaves the docomposers at about 70 - 100°C and is expected to be fully saturated with metallic mercury vapors[15]. Final carry over, therefore depends upon how far this gas is cooled to condense mercury. Inspite of a two stage cooling system in the plant under study, the gas may still contain mercury and therefore responsible for its losses in the product hydrochloric acid bbtained from this gas and waste water resulting in this production.

The final product, caustic soda leaving the decomposers may contain dispersed metallic mercury. Most of this is recovered during cooling and filteration. The final product may still contains some mercury.

Chlorine leaving the primary cells carry some brine vapors which contain dissolved mercury[16]. These vapors are retained as condensate in cooling of this gas. But waste water from pressure seals may contain mercury.

Besides the above described modes of mercury losses, it may also escape in waste water resulting from cleaning of cells, scrapped anode sludge etc. and in ventilation air from cell house.

4.2.2 Theoritical Principles Involved:

4.2.2.1. Recovery/Removal of Mercury from Brine Sludge (Chemical Oxidation Method):

As has been mentioned earlier, chemical oxidation of sludge by chlorine gas or compounds containing active chlorine converts insoluble mercury to soluble mercuric ions. The later in the presence of chloride ions in turn form a highly soluble mercuric tetra chloro complex. The hypochlorite ion (OCl^-) actually brings about the oxidation of insoluble mercury as shown below:

$$Hg + OCl^- + 3Cl^- + H_2O \rightleftharpoons HgCl_4^{--} + 2OH^-$$

$$2\ Hg^+ + OCl^- + 7\ Cl^- + H_2O \rightleftharpoons 2\ HgCl_4^{-2} + 2OH^-$$

$$Hg^{+2} + 4Cl^- \rightleftharpoons HgCl_4^{-2}$$

$$HgS + 4\ OCl^- \longrightarrow 4Cl^- + HgSO_4$$

$$HgSO_4 + 4Cl^- \longrightarrow HgCl_4^{-2} + SO_4^{-2}$$

Filterate of the treated sludge which contains dissolved mercury may be suitable for recycling to brine electrolysis cells where metallic mercury is recovered by electrolysis. Parameters which may play important role in the oxidation are oxidant dose and reaction time.

4.2.2.2 Recycle of Liquid Streams:

The filterate of the treated sludge or any other liquid stream containing mercury can be recycled to cells as long as such streams do not contain undesirable impurities and beyond tolerable limits. Impurities to be controlled in brine are calcium, magnesium, iron, free chlorine, chlorate (ClO_3^-) and sulfate (SO_4^{-2}). Impurities such as calcium, magnesium iron and several other metals may lower the over-voltage of hydrogen. This leads to evolution of hydrogen in the primary cell and thereby increasing the chances of explosion because of the excessive hydrogen in chlorine. Combination of two or more metals may have synergistic effect[3]. While the exact mechanism of this effect of impurities on hydrogen evolution is not fully understood, it is possible that certain impurities reduce the ability of the freshly deposited sodium to mix with the bulk of mercury[3]. This would cause an increase in sodium activity at the mercury-brine interface, raise the sodium deposition potential and thus favor hydrogen evolution.

Free chlorine and chlorate are interrelated in affecting the electrolysis in the sense that excessive concentration of free chlorine can increase the chlorate content which adversely affects the graphite consumption[3].

Control of the sulphate is important because a variation in sulfate concentration can vary calcium concentration which will create problems as mentioned earlier.

It is therefore important that while performing experiments on sludge oxidation the quality of filterate is also measured. Also any liquid stream which can possibly be recycled must always be monitored for the quality before getting mixed with the brine.

4.2.2.3 Mercury Recovery from Hydrogen Gas by Adsorption on Activated Carbon Bed:

Adsorption of mercury vapors (solute) in hydrogen carrier gas on activated carbon bed needs parametric studies and also the information on bed saturation time. Since adsoprtion is a surface phenomenon, one of the important parameter for adsorption studies is the surface characteristics of the activated carbon particles. Particle size therefore becomes an important parameter. Lower the particle size, higher the surface area and therefore more adsorption. However, lower particle size will result higher pressure drop. Therefore an optimum particle size should be chosen. Other important parameter with respect to the adsorbent is porosity. Higher the porosity, more surface is available for adsorption. Besides adsorbent characteristics other important parameters are length to diameter ratio (L/D) of the bed, flow of the gas, concentration of mercury in hydrogen gas and inlet gas and bed temperature. For the present study, gas composition and inlet gas temperature are not variable and therefore have been fixed by the process. Interference by the impurities present in the inlet gas also play an important role. Water vapor is the only likely impurity in the present (in the adsorption system) study. In conclusion, parametric study should include effect of water vapor, particle size, flow and L/D ratio on the adsorption rate.

Regarding bed saturation, both time and amount of mercury adsorption are important. For this it is important to know the concentration profile of mercury in outlet stream. This is generally known as 'breakthrough curve'. The shape of a breakthrough curve greatly influence the operating method of a fixed-bed adsorber.

For understanding a breakthrough curve, let us consider the case of a binary solution, a gas containing a strongly adsorbed solute at a concentration C_0, such as mercury vapor in hydrogen gas. The solution is passed through an adsorbent bed initially free of adsorbate, say from the top of the bed downwords. The upper most layer of solid, in contact with the strong solution entering, at first adsorbs solute rapidly and effectively, and what little solute is left in the solution is substantially removed by the layers of solid in the lower part of the bed. The outlet gas from the bed is practically solute-free. The distribution of adsorbate in the solid bed is indicated in the sketch in the upper part of Fig. 4.2 at (a), where the relative density of horizontal lines in the bed is meant to indicate the relative concentration of adsorbate[17]. The upper most layer of the bed is practically saturated, and the bulk of the adsorption takes place over a relatively narrow 'adsorption zone' in which the concentration charges rapidly as shown in the figure. As solution continues to flow, the adsorption zone moves downwards as a wave. At (c) the lower portion of the adsorption zone has just reached the bottom of the bed, and the concentration of solute in the effluent has suddenly risen to an appreciable value C_c for the first time. The system is said to have reached the 'break-point'. The solute concentration in the outlet now rises as the adsorption zone passes through the bottom of the bed and at (d) has substantially reached the initial value C_o. The portion of the outlet concentration curve between position (c) and (d) is termed as 'breakthrough' curve, It is important to mention that if the solute is being adsorbed adiabatically and a significant heat of adsorption is involved, a temperature wave flows through the bed in a manner somewhat similar to the adsorption wave, and the rise in temperature of the bed at the fluid outlet may sometimes be used as a rough indication of the break-point. In case of low solute concentration, as in our case the heat involved is generally not significant and therefore the ~~tem~~ temperature rise may not be noticeable. For practical purposes the break-point can be fixed any where on the curve depending upon the allowable concentration of the solute in the outlet gas. Once the shape of the curve after the breakpoint is obtained, use of two (or more) bed in series or single bed can then be decided depending upon whether the shape of the curve is shallow or almost parallel to the concentration axis. Use of three or multistage cascade systems have been suggested for cases involving shallow breakthrough curve[18]. For determining the amount of adsorbent needed for a given duty, breakthrough point and breakthrough curve are needed.

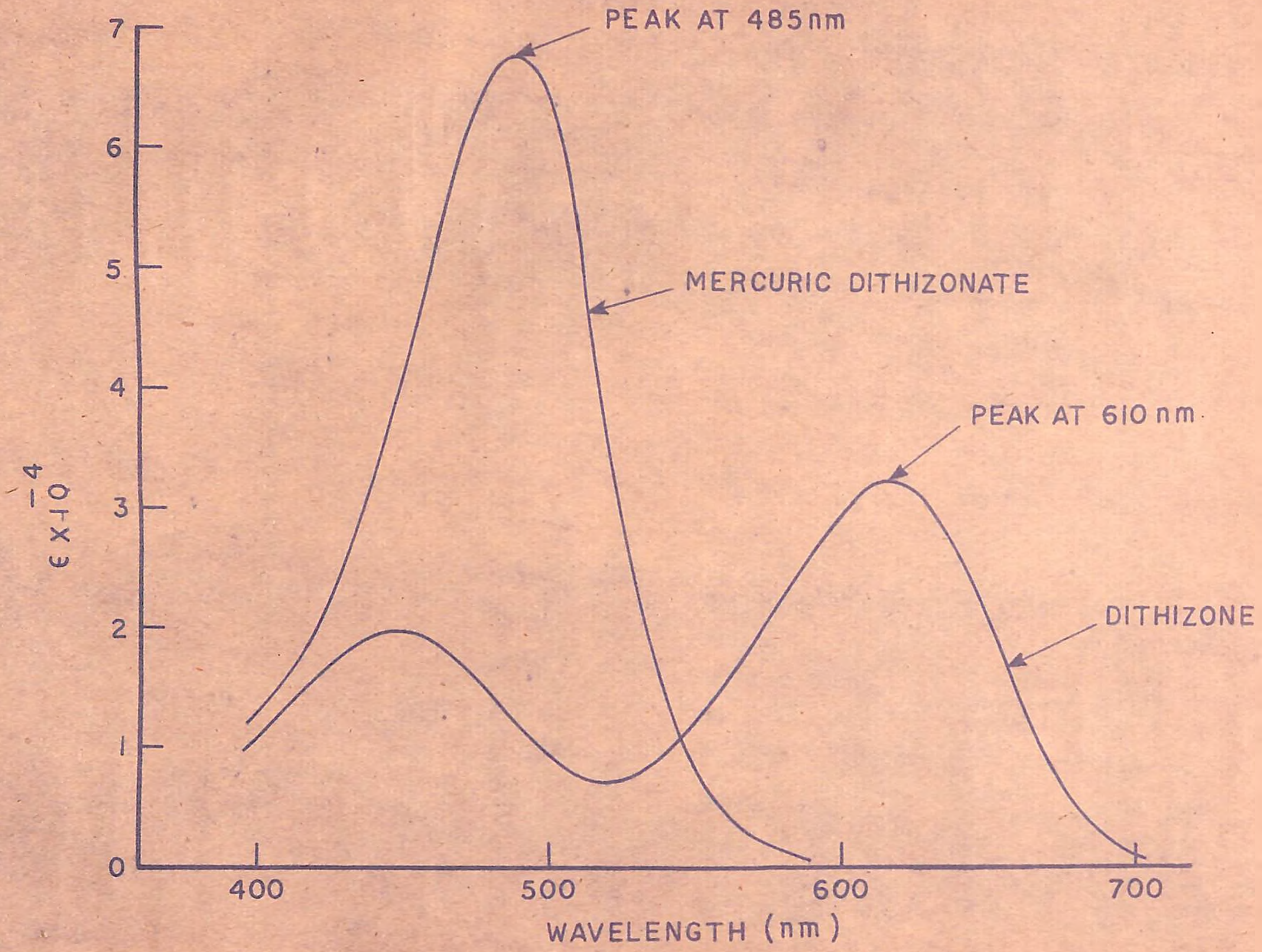


Fig. 4.1 Molar extinction coefficient curves of dithizone and mercuric dithizonate complex in CCl_4. (DATA FROM: E. B. SANDELL, COLORIMETRIC DETERMINATION OF TRACES OF METALS)

EXPERIMENTS ON MERCURY BALANCE

5. EXPERIMENTS ON MERCURY BALANCE:

5.1 Balance Procedure:

A mercury balance was made to identify major loss points in the plant. This balance was made on the mass basis and involved measuring concentration of mercury and quantity of each possible source and there by giving the mass of mercury lost, at various loss points. This total loss per unit time was compared by the mercury inventory of the plant.

5.2 Mercury Analysis:

Dithizone colorimetric method mentioned earlier was used for mercury analysis. All the reagents and solvents were of analytical grade. Bausch and Lomb's spectronic 20, spectrophotometer was used for the color intensity measurements.

Various steps involved in mercury analysis and spectrometer calibration have been diagramatically shown in Fig. 5.1. The detailed procedure is given below :

i) Dithizone solutions of different color intensities were obtained by diluting a 0.001% (w/v) solution of dithizone in carbon tetra chloride. Absorbances of these solutions were measured at 485nm and 610nm wavelengths. The curve required for excess dithizone correction was then obtained by plotting absorbance values obtained at 485nm versus those obtained at 610nm.

Results of this measurement are given in table 5.1 and figure 5.2.

ii) A known quantity of the unknown sample was taken in a beaker and treated with concentrated nitric acid to dissolve mercury. This mixture was then filtered and the residue was washed with distilled water. Washings were retained in the filterate. In case of gaseous samples a known quantity of gas was passed through acidified potasium permangnate solution to retain and dissolve mercury. Excess of KMnO4 was neutralised with $NH_2OH.HCl$. Dilute NH_4OH solution was added to the resulting filterate or colorless solution in case of gaseous sampling to bring pH to about 8 followed by addition of $NH_2OH.HCl$. pH of the resulting solution was again brought to about 1.5-2.0 with dilute H_2SO4. After adding EDTA solution, the contents of the beaker were transferred to a separating funnel. About 1-2 ml. of dithizone solution (0.001%, (w/v)) was added to this and the mixture was shaken vigorously. The orange yellow complex, which formed the organic layer was separated in a volumetric flask. This process of dithizone addition and separation of complex was continued till no orange yellow complex was obtained (i.e. organic layer remained green), Carbon tetra chloride was then added (if required) to the extracted complex to make the volume up to the mark in the flask. Transmittance of this complex solution of known volume was measured at 485nm and 610nm. A blank run was also performed to take care of any mercury present in reagents and chemicals etc. used for analysis. The values of the absorbances corresponding to the transmittance values obtained from the instrument were calculated from the relation[13]

Absorbance = Log (1/Fractional Transmittance)

iii) <u>Calculation:</u>

For illustration purpose calculation for a solid sample is described here.

If we assume quantity of sludge sample = m gms.

Volume of the extracted complex = Vml.

Absorbance for sample at 485nm = A_{485}.

Absorbance for sample at 610nm. = A_{610}.

corresponding values for blank = B_{485} and B_{610}.

Excess dithizone corrections corresponding to A_{610} and B_{610} from fig. 5.2 = A'_{485} and B'_{485}

Then the net absorbance of the complex (formed from mercury present in the sample only) will be

$$= (A_{485} - A'_{485}) - (B_{485} - B'_{485})$$

$$= \Delta A - \Delta B$$

Therefore, mercury concentration in the sludge sample

$$= \frac{a \times V}{m} \text{ microgms/gms.}$$

Where 'a' is the conc. of mercury in the complex read from the calibration curve (fig. 5.3) corresponding to ($\Delta A - \Delta B$).

iv) Calibration Curve :

(For the spectrophotometer giving mercury conc. versus net absorbance).

A solution of mercuric chloride containing 0.001% (w/v) of mercury was prepared in distilled water. Starting with different quantities of this solution extraction with dithizone was done as described earlier to get the complex. In each case the concentration of mercury in "$\mu g/ml.$" in the complex was calculated from the quantity of mercury in the standard solution taken and volume of the complex. In real practice, for convenience, complex was extracted in 25 ml. capacity volumetric flasks and carbon tetra chloride was used to make up the volume of extracted complex to a constant volume of 25ml. These values of mercury conc. in complex were plotted against the corresponding (ΔA - ΔB) values to get a calibration curve for the spectrophotometer. Results are given in table 5.2 and figure 5.3.

To check the validity of the curve and also possible drift, the calibration of the instrument was checked periodically. These repeat points are shown in table 5.3 and also in Fig. 5.3. The values of molar extinction co-efficient 'ε' for mercuric-dithizonate in carbon tetra chloride was also calculated from this curve as follows :

From the relation

$$A = \epsilon \times c \times b$$

We have for the present case in which b = 1 cm. (diameter of the sample tube used for intensity measurements)

$$A = \epsilon \times c$$

or $A = \epsilon \times 1$, where c = 1 moles/Litre in this case .

Therefore 'ϵ' for mercuric dithizonate is absorbance of a solution containing 1 mole/Litre or 710.6 gpl. (710.6 being molecular wt.) of this complex .

NOW from fig. 5.3 , we have

1 μg/ml. of mercury has 0.3 absorbance

or $\frac{710.6}{200.6}$ μg./ml. of mercuric dithizonate has 0.3 (since by stochiometry 710.6 gms. of mercuric dithizonate = 200.6 gms. Hg.)

or 3.54 μg./ml. of complex has 0.3 absorbance

or 3.54×10^{-3} gms./litre has 0.3 absorbance

Hence absorbance of 1 molar complex solution i.e. Solution containing 710.6 gms./litre will be =

$$= \frac{0.3 \times 710.6}{3.54 \times 10^{-3}} = 60220$$

This value of 'ϵ' was found to be appx. 11 % less than 6.75×10^4 reported in literature (Fig.4.1) at 485 nm .

An estimate was also made for possible error if the excess dithizone correction would have not been made. It was found that the maximum excess dithizone correction encountered during analysis of samples in this study was $\leq$ 0.047, in terms of absorbance or $\leq$ 0.17μg/ml. of mercury concentration in the complex. Had this correction not been made the error would have been $\leq$ 17% for mercury concentration of $\geq$ 1μg./ml. in the complex. In other words the values of mercury concentrations in samples would have been over estimated by $\leq$ 17% then those actually obtained with due consideration to excess dithizone correction.

5.3 Assessment of losses:

(i) General Description:

Mercury loss assessment requires (i) Avg. mercury concentration, and (ii) quantity of the corresponding liquid stream/sludge/gas involved. Sampling was done to cover time or any other variation such as change in plant conditions, which can affect mercury loss. For obtaining a better statistics a relatively large number of samplings were done for those loss points where these variations were frequent.

Although the major culprit responsible for Hg. loss was soon identified, efforts were continued to reveal the complete distribution for academic interest.

(2) Sampling and Quantification:

A list of probable loss points in the plant was prepared in consultation with the plant experts before making measurements. These points are given below :

(A) Cell House:

Graphite sludge and cell house garbage, cell cleaning waste water and cell house air.

(B) Brine House :

Brine sludge and waste water.

(C) Hydrogen and Hydrochloric Acid Section:

Condensate from cooler, product hydrochloric acid and waste water resulting from scrubbing of the uncondensed gases in HCl production.

(D) Chlorine Section :

Waste water from pressure seals.

(E) Caustic Soda Section :

Product caustic soda.

A detailed description of study conducted for sampling and quantification follows:

(A) Cell House:

(i) Graphite sludge & cell House Garbage:

Each time an anode assembly was scrapped, a composite sample of the resulting graphite sludge was made by collecting several samples from various places of the heap, grinded and thoroughly mixed before analysis. Quantity of this sludge was obtained by actual weighing. This was repeated for sludge resulting from anode assemblies corresponding to different cells. Sampling and quantification of the garbage removed from the cell house floor was done in a similar manner.

(ii) Cell Cleaning Water

At the time of cell cleaning samples were collected from the resulting waste water at different intervals of time and each time flow rate was also measured. Since erratic variation was observed both in mercury concentration and flow of the waste water, the product of mercury concentration and flow was plotted against time and loss was computed from the area under the curve. Since any negligence while cleaning was expected to effect the Hg. loss, several cleanings of different cells and different cleanings of the same cells were taken.

(iii) Cell House Air :

Method prescribed by ISI[12] was used for sampling. A known quantity of mercury bearing air was sucked and passed through acidified $KMnO_4$ solution to dissolve mercury. This resulting solution was analysed for mercury.

Samples were collected from different places in the cell house to take care of any non-homogenity in Hg. conc. in the air and at different times to cover effect of atmospheric temperature. Variation from season to season was also expected but since mercury loss involved was practically negligible, these were not studied.

(B) Brine House:

(i) Sludges:

A composite of four samples collected at different times in 24 hrs. was made for cake resulting from brine recovery drum filter. The sample collected at any time was in turn a composite of several samples collected from different portions of the cake strip.

It was observed that the cake thickness did not change during the course of experiments. In such cases if :

M - Average Cake Mass, gm./cm^2.
r - radius of the drum, cm.
b - width of filter cloth, cm.
w - revolutions of the drum per hour.

Then the quantity of cake formed in tones/day will be :

$$Q = Mx(2\pi r wb) \times 24 \times 10^{-6}$$

From the analysis of the composite sample and quantity of cake obtained from the expression given above, it was found that there was no significant variation both of the, conc. as well as quantity and hence in Hg. loss.

Brinesludge, removed from sludge pits and disposed as solid waste at the time of their cleanings, was also taken into account. A composite sample of the sludge collected from various places along the length, width and depth in the pit was made just before starting the cleaning of pit. This was done for both the existing pits and also for different cleanings of the same pit. Quantity of the sludge removed from these pits was calculated from its masured density and volume.

Sludge removed from saturator at the time of cleaning was also studied in a simibar manner.

Due to practical difficulties and uncertainties of power failures, their effect on mercury loss in brine sludge was obtained from the analysis of sludge resulting from settler drainings. It should be noted that settler is the only unit in brine house from where practically all the sludge formed as a result of brine refining operations, is removed.

Analysis of this sludge after power failures showed that more than 99% of the mercury present was in insoluble form. Any recovery of this mercury therefore with the brine recovered from this sludge by decantation and filteration, was not possible. This means that the loss due to power failures, even though determined by the analysis of settler sludge, was additional loss in this section. For determing this loss, therefore hourly samples of settler draining sludge were collected for several hours after a power failures and the same was done for a number of power failures. Quantity of settler draining sludge was estimated by three independent methods. Variation in sludge quantity obtained by these methods was less than 2%. Since the sludge is formed due to the impurities in the salt, in the first method the quantity of sludge was calculated from the quantity and quality of salt and chemicals consumed for brine resaturation and purification.

Second method involved simulation of the settler unit. For this purpose a known volume of the treated brine from inlet to settler was collected and impurities was allowed to settle under similar conditions. Total quantity of sludge was then calculated from the quantity of sludge settled from a known volume and brine flow to settler.

In the third method, a known quantity of the resaturated brine was collected from saturator and chemicals as per requirement of the actual process were added to remove the impurities. Precipitats thus obtained were allowed to settle. Quantity of the sludge was again calculated from the quantity of precipitates, brine flow and volume taken for simulation.

Mercury loss in sludge due to power failure was finally calculated graphically in a manner similar to that used for cell cleaning waste water.

(ii) Waste Water:

Samples were collected from the waste water resulting from brine house at different time and for several days to get a better statistics. Flow was measured by salt dilution method[19]. This method involved addition of a solution of iron, at a known flow rate to the stream whose flow was to be measured. Concentration of iron was then determined at point down stream to the point of iron solution addition. Flow of the stream was then calculated from the concentration of iron in solution which is added, in the stream without addition of iron solution, at the down stream point after addition of this solution and flow of solution added by simple mass balance for iron.

(C) **Hydrogen and Hydrochloric Acid Section:**

Condensate from the Hydrogen cooler was sampled and flow was obtained.

Product Hydrochloric acid was sampled at different time of a day for several days and quantity of the acid produced was obtained from daily production figures.

Waste Water resulting from scrubbing-s of the uncondensed gasses in HCl Production was analysed. Flow was obtained by salt dilution method.

(D) **Chlorine Section:**

Waste Water from pressure seals was studied as usual.

(E) **Caustic soda section:**

Samples of the product caustic soda going to storage tank were collected. Quantity of caustic soda was obtained from average production figures of the plant.

5.4 RESULTS:

It is important to mention here that due to certain confidential information about the host organization raw data are not being presented. Instead a statistical summary has been given in table 5.4.

The total loss of mercury per day was compared with the inventory of mercury and it was found that losses measured accounts for about 95% of the loss in recorded inventory for the last 6 years.

It should be mentioned here that host organization has an excellent maintenance programme. This cuts down the losses from various possible points to a drastic amount. This is one of the reason that the plant is one of the lowest mercury loss plant in the country.

It can be seen from the results in table 5.4 that the main culprit responsible for mercury loss is brine sludge accounting for 87.9% of the total loss followed by waste water from HCl plant (4.4%) and cell cleaning waste water (3.1%).

Detailed study is therefor desired for identifying a practical & feasible method for recoverying mercury from brine sludge and for optimizing various parameters involved.

In the other two cases, due to small quantity of mercury involved it was decided that for cell cleaning waste water possibilities of its recycle or reuse in the plant should be explored and for waste water resulting from HCl plant, hydrogen gas itself should be treated so as to eliminate mercury not only from this waste water but also from product HCl and other points in Hydrogen and Hydrochloric Acid section.

TABLE 5.1.

Absorbance of different color intensity Dithizone Solutions at 610nm and 485nm.

S. No:	Absorbance of dithizone solutions			
	At 610 nm.		At 485 nm.	
	Transmittance*	Absorbance**	Transmittance	Absorbance
1.	0.985	0.0066	0.980	0.0088
2.	0.980	0.0088	0.975	0.0110
3.	0.950	0.0223	0.955	0.0200
4.	0.905	0.0434	0.935	0.0292
5.	0.830	0.0809	0.880	0.0555
6.	0.775	0.1107	0.840	0.0757
7.	0.705	0.1518	0.790	0.1024
8.	0.590	0.2291	0.710	0.1487

* From Instrument. (Fractional Transmittance).

** Absorbance = Log (1/Fractional Transmittance).

TABLE 5.2

Calibration Data for the Spectro Photo Meter

S.No:	Conc. of Hg in Complex (ug/ml.)	ABSORBANCE OF COMPLEX SOLUTION				Excess dithizone correction for A_{610} from Fig.5.2, A'_{485}	Net Absorba $(A_{485} - A'$ $-(B_{485} - B$
		AT 485 nm		At 610 nm			
		Transmittance	Absorb. (A_{485})	Transmittance	Absorb. (A_{610})		
1.	0.2	0.775	0.1107	0.890	0.0586	0.0367	0.0639
2.	0.4	0.675	0.1707	0.890	0.0586	0.0367	0.1239
3.	0.6	0.585	0.2328	0.875	0.0580	0.0414	0.1813
4.	0.8	0.505	0.2967	0.890	0.0506	0.0367	0.2499
5.	1.0	0.480	0.3188	0.930	0.0315	0.0246	0.2841
6.	1.2	0.415	0.3820	0.910	0.0410	0.0306	0.3413
7.	1.4	0.310	0.5086	0.860	0.0655	0.0461	0.4524
8.	2.0	0.250	0.6021	0.910	0.0410	0.0306	0.5614
9.	4.0	0.055	1.2596	0.910	0.0410	0.0306	1.2189

For Blank run: B_{485} = 0.0246

B_{610} = 0.0155

B'_{485} = 0.0145

Table 5.4.

Mercury Loss from Various Source Points of the Chlor-Alkali Plant

Name of section	Modes of Mercury Loss	Mercury Conc. (Mean $\pm \sigma$)	Quantity of the corresponding sludge/liquid stream/gas etc. (Mean $\pm \sigma$)	Mercury Loss (kgs/day) (Mean $\pm \sigma$)	Number of Samples	% of the Total Loss
(1) Cell House Section	(A) Solid Sludges : (i) Graphite sludge	(1039 ± 115.9) gms/tone	(0.107 ± 0.016) Tons/day	0.111 ± 0.021	13	1.1
	(ii) Floor sweepings	(9034.5 ± 1796.2) "	$(8.2 \pm 1.74) \times 10^{-3}$ "	0.074 ± 0.022	20	0.7
	(B) Liquid Stream: (i) Cell cleaning wastewater	(1-450) gms/M^3	(3-12) M^3/hr	0.319 ± 0.114	28	3.1
	(C) Ventilation air	$(3.0 \pm 0.67) \times 10^{-6}$ gms/M^3	$3.024 \times 10^6 M^3$/day	0.009 ± 0.002	16	0.1
(2) Brine House Section	(A) Brine Sludge (Wet basis)	(161.9 ± 18.7) gms/tone	(16.88 ± 1.76) tones/day	8.93 ± 0.401*	26	87.9
	(B) Waste Water	(0.24 ± 0.06) gms/M^3	$(7.48 \pm 0.51) \times 24 M^3$/day	0.043 ± 0.011	40	0.4
(3) Hydrogen and Hydrochloric Acid Section	(i) H_2 cooler condensate	(0.31 ± 0.09) "	$(0.045 \pm 0.012) \times 24 M^3$/day	$(0.34 \pm 0.14) \times 10^{-3}$	7	-
	(ii) Product HCl (100% basis)	(1.21 ± 0.05) gms/Tone	63.6 tones/day	0.077 ± 0.003	10	0.8
	(iii) Waste Water	(0.58 ± 0.05) gms/M^3	$(32.21 \pm 1.35) \times 24 M^3$/day	0.448 ± 0.043	40	4.4
(4) Chlorine Section	Waste Water from Pressure seals	(0.19 ± 0.06) gms/M^3	$(1.088 \pm 0.058) \times 24 M^3$/day	0.006 ± 0.002	7	0.1
(5) Caustic Soda Section	Product Caustic Soda (100% basis)	(1.17 ± 0.08) gms/tone	120 tons/day	0.140 ± 0.010	10	1.4
			T O T A L	10.16 ± 0.42		100.0

* Mercury loss due to power failures included.

$$\sigma \text{ (standard deviation)} = \sqrt{\frac{\Sigma(\bar{x} - x_i)^2}{n-1}}$$

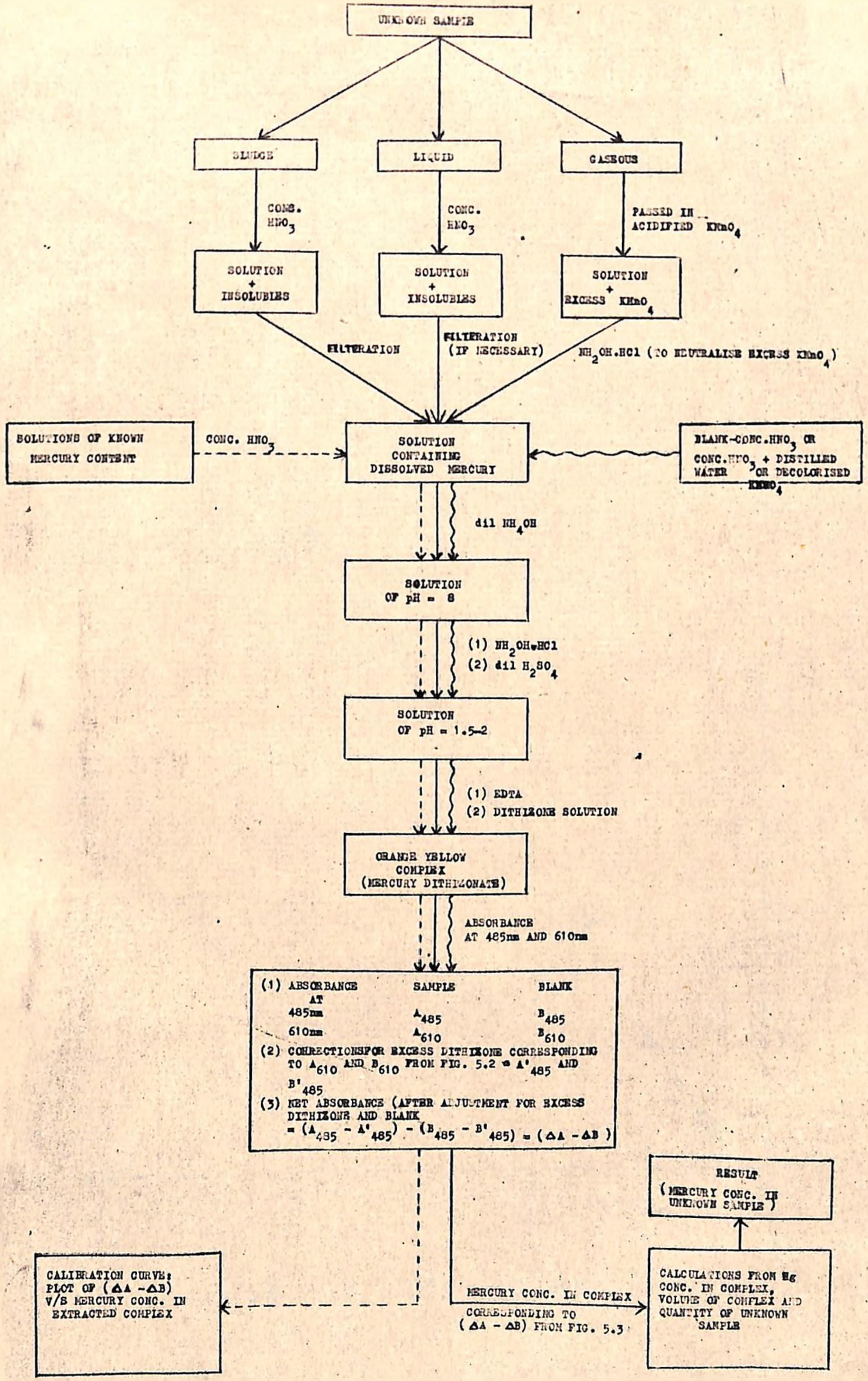


FIG. 5.1 STEPS FOR MERCURY ANALYSIS

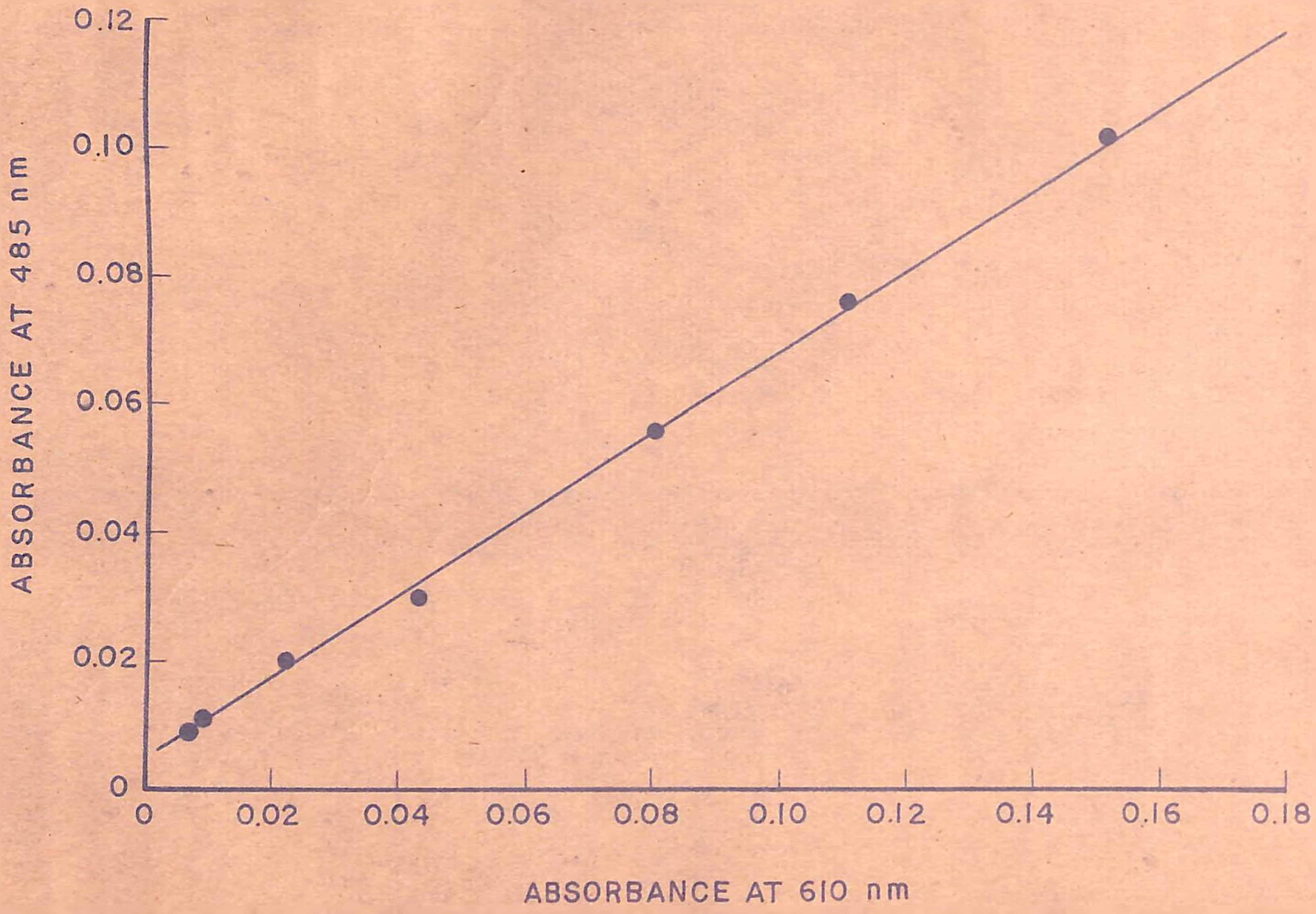


FIG. 5.2 EXCESS DITHIZONE CORRECTION CURVE (ABSORBANCE OF DIFFERENT COLOUR INTENSITY DITHIZONE SOLUTIONS AT 485 AND 610 nm).

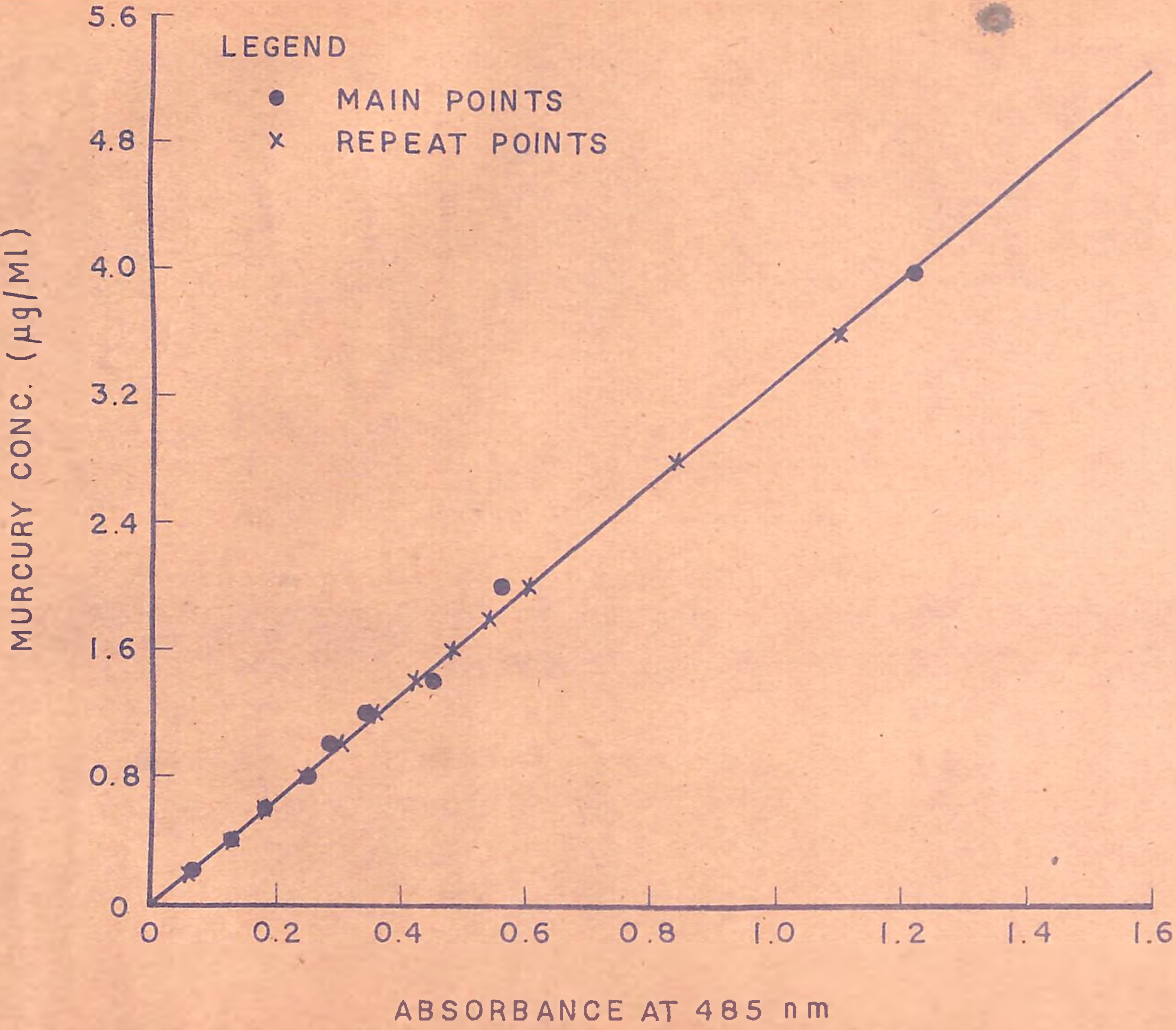


FIG. 5.3 SPECTROPHOTOMETER CALIBRATION CURVE

MERCURY RECOVERY FROM BRINE SLUDGE

6. MERCURY RECOVERY FROM BRINE SLUDGE:

6.1 Experimental Programme:

6.1.1 Recovery Techniques:

As described earlier brine sludge results from brine purification operations. Besides mercury and entrapped brine, sludge consists of calcium sulfate, calcium carbonate, Magnesium hydroxide and silica as insolubles. The exact forms of mercury present in this sludge are not known. However the possible forms as reported in literature[6], are Hg°, Hg^{+} and mercuric sulfide.

Two potential techniques, namely roasting and chemical oxidations were tried in this study. Roasting involves heating of the sludge to high temperature and condensation of the emerging gases to give metallic mercury. Chemical oxidation converts mercury to soluble mercuric ions, which come along with the filterate. This filterate can be recycled to brine stream going to cell house as long as its quality is maintained. Since chlorine is a part of brine, therefore chlorine or chlorine compounds as oxidants are preferred to other oxidants which might create some complication, to the quality of brine and thereby to electrolysis. Various promising chlorine based oxidants are :

(i) $NaOCl$ (ii) $CaOCl_2$

(iii) Cl_2-Water (iv) Cl_2-gas

6.1.2 Experimental Techniques and Results :

General steps followed have been shown in Fig 6.1 . For roasting technique cost feasibility calculations were made by estimating the fuel cost required to heat the sludge to a reported tempreture of 750–760°C . For chemical oxidation, experiments were conducted with various chlorine based oxidants to find the percentage mercury recovery, optimum dose of oxidant required and amount of impurities (mainly Ca and Mg) dissolved along with mercury under optimum conditions.

For comparison of the various alternatives, the ratio of Hg recovered to the cost was calculated in each case. Since the idea was to make a relative comparison, operating costs were not taken into account . Also in case of NaOCl, cost of oxidant along was considered and the impurities (Ca and Mg) introduced by this treatment were ignored . This is because, cost of NaOCl alone was quite high as compared to Hg recovery . Since $CaOCl_2$ and Cl_2 water are being rejected as wastes in the plant, no oxidant costs were considered in these cases . However the cost of chemicals required to remove Ca and Mg introduced in the filterate were considered. In case of Cl_2 gas only preliminarly experiments were conducted to have an approximate idea of the oxidant dose required, impurities which get dissolved and percentage Hg recovery. This is because of the fact that the brine sludge obtained in the form of cake from drum filter is very thick and chlorination of this cake as such is not possible. This dilution results dilute brine which is not suitable as such. However for comparison it was kept in mind that chlorination of the sludge (rather than cake) would not require such dilution and also chlorine gas addition will avoid any dilution which the other oxidant create because they are added as solutions. Both, cost of oxidant as well as chemicals required for removing Ca, Mg was considered in this case.

Finally the ratio of recovery/cost obtained was compared and the method, giving highest value was selected for studying. Optimization of parameters involved, impurities likely to be present with respect to brine quality etc.

6.2 Chemical Oxidation Using Chlorine Compounds:

6.2.1 Oxidation using NaOCl, $CaOCl_2$ and Cl_2 water:

A known quantity of the brine sludge (drum-filter cake) was taken and mixed with a known quantity of the solvent (oxidant) in a beaker provided with a magnetic stirrer. Several experiments, under different conditions were conducted with each of the oxidant. The treated sludge at the end of each of these experiments was filtered, washed with distilled water and the resulting filterate was analysed for its mercury conc. Percentage recovery of Hg was also calculated in each case from the initial Hg conc. of the untreated sludge.

For parametric study following parameters were studied :

1. Volume of Oxidant.
2. Reaction time

First experiments were conducted using a standard classical statistical method whereby one parameter is fixed and effect of other parameter is studied. These experiments were followed by three level factorial experiments to find optimum values of parameters. Results are given in tables 6.1, 6.2 and 6.3. The filterate of the experiments with optimum parameters was analysed for Ca. & Mg. impurities to check wheather they are within permissible limits or not. Quantities of Ca, Mg introduced have been directly given in table 6.5 for relevent cases.

6.2.2 Chlorine treatment Method:

i) Experimental Set-up:

Experimental set-up is shown in Fig. 6.2.

Chlorine gas required for the experiment was taken from a clorine cylinder. The position of the chlorine cylinder valve was calibrated for chlorine flows. For a particular opening of the valve, chlorine was allowed to be absorbed in caustic soda solution of known conc. and quantity for a known time. The quantity of the chlorine absorbed in NaOH was determined iodometrically and thus chlorine flow for the corresponding valve position was obtained. This was repeated for various valve positions for calibration. A 4-liter glass flask provided with a magnetic stirrer was used as a reaction flask.

ii) Procedure:

About one kg. of the waste sludge was taken. The drum filter cake used for these experiments is very thick and direct chlorination was not possible. This cake was therefore diluted with distilled water. The diluted cake was then taken for chlorination. Chlorine gas was passed through this sludge taken in the reaction flask at a known flow rate, for a known time. After the chlorine supply was stopped agitation of the mixture was continued for about one hour. At the end of the experiment the treated sludge was filtered and the filterate was analysed for its mercury, calcium and 'Mg' concentrations. Each time when sample was to be taken out from treated sludge for analysis, Air was passed (refer Fig. 6.2) to remove chlorine which occupies the space over the sludge and was absorbed in NaOH. Percent mercury recovery was calculated from the initial Hg concs.

of the starting sludge and Hg conc. in the filterate . Results are given in table 6.4 .
Since dilution of the cake would result unnecessary dilution in brine system, no further experiments were conducted with this sludge . However the results of the preliminary experiments conducted were used for comparision with other oxidants .

6.3 Roasting :

Theoritical calculations were done to obtain the quantity of coal required to heat the sludge to 760° C for 99.8 % Hg removal . The heat requirement for this purpose was calculated for total quantity of cake to be roasted, its complete analysis and specific heats of the various species present in it . Regarding the calorific value of the coal, its conversion efficiency and margin for radiation losses used in the calculations, data were collected from the experts of the host organization . These calculations are given below :

I. Avg. analysis of the drum filter cake :

$CaSO_4$	=	10.7 %
$CaCO_3$	=	17.9 %
$Mg(OH)_2$	=	2.8 %
Insolubles	=	8.15 % (Mainly silica)
Na_2CO_3	=	0.9 %
NaCl	=	5.75 %
Moisture	=	52.8 %

II. Total quantity of cake/day = 5.73 tones (on wet basis - Method described in Chepter-V) Therefore total quantities of the various species present will be (Based on analysis given above) -

$CaSO_4$ = 613 Kgs / day

$CaCO_3$ = 1026 "

$Mg(OH)_2$ = 160 "

Insolubles = 467 "

$Na_2 CO_3$ = 52 "

NaCl = 330 "

Moisture = 3025 "

III. Heat requirement: For raising the temperature of the cake from 25°C to 760°C (Specific Heat Data taken from Lange's Hand Book of Chemistry 11th Edition, table 9.8, pp 9.120-140)

(i) Heat required by $CaSO_4$ (H_{CaSO_4})

$= M \times S \times \triangle T$

$= 613 \times 0.265 \times (760-25) = 119397$ K.Cal.

Similarily

(ii) H_{CaCO_3} = 153084 K.Cal.

(iii) $H_{Mg(OH)_2}$ up to 350°C (at 350°C it decomposes into MgO and H_2O)

$= 160 \times 0.314 \times (350-25) = 16328$ K.Cal.

(iv) Heat required by water lost in decomposition

$= M \times L$

$= 50 \times 540$ (160Kg $Mg(OH)_2$ = 50Kg H_2O)

= 27,000 K.Cal.

(v) Heat required by MgO from 350 to 760°C

$= 110.4 \times 0.209 \times (760-350)$

$= 9460$ K.Cal.

(160 Kg $Mg(OH)_2$ = 110.4 Kg. MgO.)

(vi) $H_{\text{Insolubles (Mainly silica)}}$

$= 467 \times 0.191 \times 735$

$= 65560$ K.Cal.

(vii) H_{NaCl}

$= 330 \times 0.204 \times (760-25)$

$= 49480$ K.Cal.

(viii) $H_{Na_2CO_3} = 52 \times 0.256 \times (760-25)$

$= 9784$ K. Cal.

(ix) Moisture in sludge = 3025 Kg.

it will require heat for its temperture rise from 25°C to 100°C and then for phase change at 100°C.

Hence $H_{\text{moisture}} = 3025 \times 1 \times (100-25) + 3025 \times 540$

$[(M \times s \times \Delta T) + (M \times L)]$

$= (226875 + 1633500)$ K.Cal.

$= 1860375$ K.Cal.

Total Heat required therefore (Summation of (i) to (ix)) will be = 2310468 K.Cal.

$= 2310.5 \times 10^3$ K.Cal.

After giving 50% allowance for heat losses net heat to be supplied for roasting the sludge will be $= 3465.8 \times 10^3$ K.Cal.

$$\text{Coal required} = \frac{\text{Heat requirement}}{(\text{calorific Value of Coal}) \times (\text{Conversion efficiency of Coal})}$$

$$= \frac{3465.8 \times 10^{3} \text{ K.Cal.}}{(5272.5 \text{ K.Cal/Kg})\ (0.2)}$$

$$= 3285 \text{ Kgs.}$$

$$= 3.3 \text{ tones (appox)}$$

which at the rate of Rs.150/- Tone (Rate taken from the raw-matarial section of the Host Organization) amounts to Rs. 500 (appox.) per day.

6.4 Discussion of Results:

6.4.1 Discussion:

It can be seen from Fig.6.3 that in NaOCl Oxidant treatment the recovery of Hg gradually increases with increase in oxident dose upto 5.0 ml after which any further addition of oxidant is of no use for any reaction time. Also looking at the different curves corresponding to different reaction times it is clear that after 35 minutes there is no more increase in the recovery of Hg. irrespective of the quantity of the oxidant added. The optimum condition~~s~~ is therefore 5.0 ml of NaOCl (62.3gpl available chlorine conc.) for 35 minutes for 10 gms. of cake (wet basis). Mercury Recovery being 93%.

Based on similar arguments the quantity of ca-hypo and Cl_2 water per 10gm. of cake obtained from fig.6.4 and 6.5 are 6.0 ml and 20.0ml respectively. However it is the impurities which are impartant in these cases.

6.4.2 Comparative Study:

A comparision showing results obtained with various oxidants used for mercury recovery along with cost of oxidants and chemicals required to remove impurities has been given in table 6.5.

Since $CaOCl_2$ is a waste in the plant no cost of this chemical was taken for estimation but treatment of sludge with this oxidant leads to a very high concentration of calcium and magnesium in the filterate containing recovered mercury. Also the Hg recovery is only 70%. In this case the cost of lime and soda-ash (Chemicals used for brine purification) required to remove these impurities were considered.

Chlorine water treatment of the sludge appears of no practical significance. This is because Hg recovery is only 56.5%, and also since the total quantity of chlorine water required for this treatment is a large quantity.

It is clear from table 6.5 that the ratio of the cost of mercury that can be recovered to the cost of chemicals required is highest in case of chlorine treatment of sludge. Moreover the treatment steps involved are similar in case of all chemical oxidants and also if chlorination of the sludge is done before it is sent to drum filter for brine recovery this existing filter can be used to filter the chlorinated sludge . A detailed study for obtaining control parameters involved was conducted for chlorine technique.

6.5 Chlorine treatment Technique for Mercury Recovery :

6.5.1 Optimization of Parameters :

Since the quality of the filterate of chlorinated sludge is very important as it is to be recycled to electrolysis cells, the basis of obtaining optimum values of the parameters involved was not only maximum mercury recovery with minimum chlorine dose in minimum time but also the conc. of other impurities which get dissolved and enter in the filterate . From the results of the experiments conducted with diluted cake it was seen that Magnesium present in the sludge as $Mg(OH)_2$ also gets dissolved alongwith mercury to significant levels as a result of Chlorination. A calculation was therefore made to estimate the allowable Mg conc. in the filterate to be recycled. This was done knowing the maximum tolerable conc. of magnesium in feed brine to electrolysis cells, its flow and approx. quantity of the filterats that will be obtained in chlorination techniques . It was found from these calculations that in order to keep magnesium conc. in feed brine below a 5 mg/l increase , chlorinated sludge filterats with a Mg conc. upto 500-550 mg/l (as MgO) can be recycled. Keeping this objective in mind following experiments were conducted for parameter optimization.

(i) In the first set of experiments, keeping sludge quantity and chlorine flow as constant, chlorination time was varied and the filterate of the treated sludge in each case was analysed for its Ca, Mg, SO_4^{--}, NaCl, Free Chlorine, ClO_3^- and mercury concs. Results are given in table 6.6 and the variation of the conc. of Ca, Mg and % Hg recovery with time has been shown in fig.6.6. It was found from these results that for a chlorine flow of 0.65 gpm a chlorination for around 5 minutes leads to the levels of magnesium mentioned above. Ca and other species are within tolerable limits.

(ii) In the second set of experiments keeping the sludge quantity and chlorination time constant (5 minutes) Chlorine flow was varied. However, analysis of the treated sludge filterate was confined to Ca, Mg and mercury only, as the results of the first set of experiments indicated that other species are hardly affected by this treatment. Results are given in table 6.7 and also shown in fig. 6.7. It was found from these results that for 1.09 kg of sludge a chlorine flow of 0.62 gms/minute for 5 minutes leads to a MgO conc. of 500 mg/l in the filterate.

(iii) In the third set of experiments the quantity of sludge (1.09 kg), Chlorine flow (0.62 gms/minute) and chlorination time (5 minutes) were kept constant and the agitation of the sludge after 5 minutes of chlorination was continued. Filterate of this treated sludge after different times of agitation was analysed for various species.

Results are given in table 6.8 and shown in fig. 6.8.

As can be seen from table 6.8, it was observed that simple agitation of the chlorinated sludge after the chlorine supply is stopped does not lead to any more increase in the conc. of impurities in the filterate but the recovery of Hg gradually increases and reaches a maximum of 83.9%, 50 minutes after the chlorine supply is stopped. It should be noted here that the sludge to be treated is always alkaline i.e. OH^- ions are always present in the aqueous phase and chlorination is likely to produce OCl^- ions in this phase. That is to say that even if Chlorine supply is stopped these OCl^- ions should be able to dissolve Hg.

(iv) Based on the above experiments conducted with 1.09 kg. of brine sludge, it could be concluded that the optimum values of the parameters are as given below :

Chlorine flow = 0.62 gms/minute.

and chlorination time (5 minutes) were kept constant and the agitation of the sludge after 5 minutes of chlorination was continued. Filterate of this treated sludge after different times of agitation was analysed for various species.

Results are given in table 6.8 and shown in fig. 6.8.

As can be seen from table 6.8 , it was observed that simple agitation of the chlorinated sludge after the chlorine supply is stopped does not lead to any more increase in the conc. of impurities in the filterate but the recovery of Hg gradually increases and reaches a maximum of 83.9%, 50 minutes after the chlorine supply is stopped. It should be noted here that the sludge to be treated is always alkaline i.e. OH^- ions are always present in the aqueous phase and chlorination is likely to produce OCl^- ions in this phase. That is to say that even if Chlorine supply is stopped these OCl^- ions should be able to dissolve Hg.

(iv) Based on the above experiments conducted with 1.09 kg. of brine sludge, it could be concluded that the optimum values of the parameters are as given below :

Chlorine flow = 0.62 gms/minute.

Chlorination time = 5 minute

Extra agitation time = 50 minutes.

(v) To check the above results and also to search a batter optimum set of conditions around the values obtained by above experiments 3^3 factorial experiments were conducted. Results are given in table 6.9. It was found from these results that a chlorine flow of 0.58 gms/minute for six minutes and extra agitation of 50 minutes gave the same recovery as obtained by previous optimum. Magnesium conc. in the filterate however becomes higher then the corresponding to earlier optimum point. Hence the earlier optimum conditions were taken to be the final. Based on these results and the total quantity of the sludge to be treated, the requirement of chlorine/day was calculated as follows :

Chlorine required per kg of wet sludge

$= \frac{0.62\times5}{1.09}$ gm chlorine / kg of sludge.

= 2.844 gms chlorine / kg of sludge.

= 2.844 kgs. chlorine / tone of sludge

Since sludge / day from settler drainings is 84 tones (Method of sludge estimation described in chapter - V), chlorine / day required will be

= 2.844 x 84 kgs = 240 kgs. approximately.

6.5.2 Effect of Changes in Initial Conc. of Mercury in the Sludge on Mercury Recovery:

For this purpose, keeping the sludge quantity and the optimum conditions to remain the same as mentioned in the preceding sections experiments were repeated with different starting conc. of Hg in the sludge. Results are given in table 6.10. These results showed that the recovery of mercury is independent of initial Hg conc. in the sludge.

6.5.3 Extraction of soluble Mercury from Chlorinated Sludge:

The percent mercury recovery mentioned under section 6.5.1 actually refers to the part of the insoluble mercury present in brine sludge which gets converted into soluble forms. In other words the 83.9% mercury recovery by chlorination of the sludge simply indicates the conversion of 83.9% of mercury to soluble forms which consequently get dissolved in the aqueous phase of the sludge.

This clearly shows that adequate washing has to be given to the chlorinated sludge after filteration to extract maximum of this 83.9%. The actual recovery therefore will depend upon how far this soluble Hg can be extracted by washing with water. To obtain optimum quantity of water required for maximum extraction, 100 gms of the chlorinated sludge was taken, filtered using ordinary filter paper in a buchnner funnel and residue was washed with known quantity of distilled water. The filterate thus obtained including washings was analysed for total Hg. Similarly starting each time with 100 gms of the chlorinated sludge the steps were repeated for varying quantities of distilled water and Hg recovery in each case was determined. Results have been given in table 6.11 and shown in fig. 6.9. As can be seen from these results that 55ml of water is able to extract 95% of the soluble Hg present in the chlorinated sludge. This means that altbough chlorine treatment converts 83.9% of the Hg in the sludge to soluble form, 95% of this 83.9% in practical will be actually recovered in the filterate to be recycled to cells, i.e. actual Hg recovery will be (0.95 x 83.9) % or 79.7% = 80% (Appox.)

The total valoume of the filterate including washing was found to be 85 ml for 100 gms of sludge.

The total quantity of sludge drained / day from settler is 84 tons on wet basis, the total filterate resulting from filteration of this sludge and washing will therefore be $\frac{85 \times 84}{100}$ M^3/day. i.e. 71.4 M^3 / day or 2.975 = 3 M^3 / hr.

For a final check the filtrate obtained from the filteration and washings of the chlorinated sludge was anlysed for its Ca, Mg, NaCl, SO_4^{--} , free chlorine and ClO_3^- contents and was found suitable for recycling to electrolysis cells with feed brine.

Table 6.1

Mercury Recovery From Brine Sludge by NaOCl Treatment

(i) Quantity of Sludge taken in each run = 10 gms(wet basis)

(ii) Available chlorine in NaOCl = 62.3 gpl.

S.No:	Run No:	Volume of NaOCl (ml.)	Reaction time (Minutes)	Mercury Recovery(%)
1	2	3	4	5
1.	2	1.0	5	23.0
2.	1	1.5	5	26.5
3.	3	2.5	5	38.9
4.	4	4.0	5	56.3
5.	8	4.5	5	63.2
6.	6	5.0	5	70.2
7.	7	6.0	5	70.2
8.	5	7.0	5	70.2
9.	9	5.0	5	70.2
10.	10	5.0	15	80.0
11.	14	5.0	20	82.5
12.	15	5.0	25	86.0
13.	17	5.0	30	90.5
14.	18	5.0	32	91.8
15.	19	5.0	32	91.5
16.	20	5.0	35	92.8
17.	21	5.0	35	92.8
18.	11	5.0	38	92.8
19.	12	5.0	38	93.0
20	13	5.0	40	93.0

1	2	3	4	5
21.	16	5.0	45	93.0
22.	22	4.7	32	88.1
23.	23	4.7	32	88.2
24.	26	4.7	35	88.4
25.	27	4.7	35	88.5
26.	24	4.7	38	88.4
27.	25	4.7	38	88.3
28.	32	5.3	32	92.1
29.	33	5.3	32	92.0
30.	30	5.3	35	92.8
31.	31	5.2	35	92.6
32.	28	5.3	38	92.9
33.	29	5.3	38	93.0

Table 6.2

Mercury Recovery from Brine Sludge by Calcium hypochlorite treatment

(i) Quantity of sludge taken in each run = 10 gms (wet basis)

Sr.No:	Run No:	Volume of Calcium-hypo (ml.)	Reaction time (Minutes)	Mercury Recovery(%)
1	2	3	4	5
1.	2	2.0	5	19.0
2.	1	3.0	5	24.3
3.	3	4.0	5	34.1
4.	4	5.0	5	43.2
5.	8	5.5	5	47.1
6.	6	6.0	5	48.5
7.	7	6.5	5	48.4
8.	5	7.0	5	48.5
9.	9	6.0	5	48.5
10.	10	6.0	15	53.3
11.	14	6.0	20	57.5
12.	15	6.0	30	63.0
13.	17	6.0	35	67.7
14.	18	6.0	37	69.7
15.	19	6.0	37	69.4
16.	20	6.0	40	70.5
17.	21	6.0	40	70.4
18.	11	6.0	43	70.4
19.	12	6.0	43	70.4
20.	13	6.0	45	70.4

1	2	3	4	5
21.	16	6.0	15	70.4
22.	26	5.7	37	67.8
23.	27	5.7	37	67.7
24.	22	5.7	40	68.6
25.	23	5.7	40	68.6
26.	24	5.7	43	68.6
27.	25	5.7	43	68.7
28.	28	6.3	37	69.7
29.	29	6.3	37	69.5
30.	32	6.3	40	70.4
31.	33	6.3	40	70.4
32.	30	6.3	43	70.5
33.	31	6.3	43	70.4

Table 6.3

Mercury Recovery from Brine Sludge by Chlorine Water Treatment

Quantity of sludge taken = 10 gm. (wet basis)

Sr. No:	Run No:	Volume of Chlorine Water(ml)	Reaction time (Minutes)	Mercury Recovery(%)
1	2	3	4	5
1.	5	5.0	10.	27.5
2.	4	10.0	10	30.9
3.	6	15.0	10	35.9
4.	1	20.0	10	42.1
5.	2	25.0	10	42.3
6.	3	30.0	10	42.1
7.	16	20.0	15	43.7
8.	15	20.0	30	48.1
9.	7	20.0	40	51.2
10.	9	20.0	50	53.7
11.	8	20.0	55	54.9
12.	12	20.0	57	56.2
13.	13	20.0	57	56.4
14.	17	20.0	60	57.1
15.	18	20.0	60	57.0
16.	10	20.0	63	56.9
17.	11	20.0	63	56.9
18.	14	20.0	65	56.8
19.	19	17.0	57	54.8
20.	20	17.0	57	54.6

1	2	3	4	5
21.	21	17.0	60	55.5
22.	22	17.0	60	55.3
23.	23	17.0	63	55.5
24.	24	17.0	63	55.7
25.	25	23.0	57	56.2
26.	26	23.0	57	56.2
27.	29	23.0	60	57.1
28.	30	23.0	60	57.1
29.	27	23.0	63	57.1
30.	28	23.0	63	57.0

Table 6.4

Mercury Recovery from Brine Sludge by Chlorine-gas Treatment

Run No:	Qty. of diluted cake Kgs.	Water Conc. (%)	Chlorine Flow gms/mt.	Chlorination time (minutes)	Total Reaction Time (mts)	Mercury Recovery (%)
1.	1.09	70.1	0.65	5	60	83.7
2.	"	"	"	"	"	83.9
3.	"	"	"	"	"	84.1
4.	"	"	"	"	"	83.8

Table 6.5

Comparative statement of the cost V/s. Hg Recovery of Various Recovery Methods.

Cake Qty. (dry) Tones/ day.	Qty. of Hg Cake Kgs/ day	Treatment ingiven to cake.	Hg Recovery (%)	Qty.of Hg Recovered. Kgs/day	Cost* of Recovered Hg Rs/day	Cost of Oxidant used			Ca Introduction in system per 10 gm. of drycake (gms)	Mg Intro. per 10gm dry cake (gms)	Total Ca Introduced Kgs/ day.	Total Mg Introduced Kgs/ day.	Lime** reqd. to ppt. Mg in (13) Kgs/day	Cost of lime Reqd. forMg removal Rs/ day.	Ca Introduced with lime used for Mg removal Kg/day.	Total Ca Introduced (12)+ (16)kgs/ day	Soda** ash Reqd. to ppt. Ca kgs/day	Cost of Soda Ash consumed. Rs/ day.	Total cost (9)+ (15)+ (19) Rs/day (÷)	Cost of Hg Recovered +cost of chemical (6)/(20)
						Qty.of oxidant Reqd. per 10 gm of dry cake	Total Qty. Reqd./ day.	Cost of Chemical Rs/day.												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
3.1	2.57	Na-hypo	93.0	2.39	191	13.3ml	4.12M^3	770	-	-	-	-	-	-	-	-	-	-	770	0.248
3.1	"	Ca-hypo	70.4	1.81	145	-	-	-	0.7187	0.0807	222.8	25.0	77.1	42	41.7	264.5	700.9	1262	1304	0.111
3.1	"	Cl_2-water	56.5	1.45	116	-	-	-	0.3355	0.0939	104.0	29.1	89.7	49	48.5	152.5	404.1	727	776	0.150
3.1	"	Cl_2-gas	84.0	2.16	173	0.1gm	31kgs	17	0.0013	0.0077	0.4	2.4	7.4	4	4.0	4.4	11.7	21	42	4.119
3.1	"	Heat	99	2.54	203	-	-	-	-	-	-	-	-	-	-	-	-	-	500	0.41

* Cost of chemicals taken from host [illegible] organization are :

Mercury	-	Rs.80,000/tone.
NAOCl	-	Rs. 3,000/tone of available chlorine
Chlorine gas	-	Rs. 550/tone.
Lime	-	Rs. 550/tone.
Soda-Ash	-	Rs. 1800/-tone.

** Based on stoicheometric calculations.

Table 6.6

Mercury Recovery From Brine Sludge by Chlorination Technique

(Mercury Recovery V/S Chlorination Time)

(i) Sludge quantity in each run = 1.09 kg (wet basis),

(ii) Moisture in Sludge-69.7%

(iii) Chlorine flow - 0.65 gms/minute.

Run No:	Chlorination Time(Mts.)	% Hg Recovery	Analysis of the Chlorinated Sludge filterate					
			Cl^- (as NaCl) gpl	Ca (asCaO) mg/l	Mg as (MgO) (mg/l)	Free Cl_2 (mg/l)	ClO_3^- (as $NaClO_3$) gpl	SO_4^{--} gpl
1	0	0	251.2	1304.0	16	Nd*	4.2130	9.5633
2	2	35.6	"	1322.8	96	213.2	4.2520	9.4754
3.	3	42.8	"	1341.3	221	408.0	4.2910	9.4591
4	4	48.1	"	1357.1	368	600.1	4.3302	9.4371
5	5	55.8	"	1379.2	550	840.0	4.3692	9.4184
6	6	61.2	"	1397.2	840	979.1	4.3981	9.3982
7	7	64.3	"	1413.2	1250	1159.3	4.4071	9.3812
8	8	68.8	"	1423.3	1790	1279.3	4.4283	9.3662
9	10	73.1	"	1432.7	2441	1380.1	4.4682	9.3542

* Not detectable.

Table 6.7

Mercury Recovery from Brine Sludge By Chlorination Technique.

(Mercury Recovery V/s. Chlorine flow)

(i) Sludge Quantity = 1.09 Kg in each run.
(ii) Moisture in sludge = 69.7%
(iii) Chlorination Time = 5 Mts.

Run No:	Chlorine Flow (gms./minute)	% Mercury Recovery	Analysis of the Filterate Ca (as CaO) (mg/l)	Mg (as MgO) (mg/l)
1	0	0	1304.0	16
2	0.458	46.3	1345.5	398.5
3	0.510	49.3	1350.0	410.0
4	0.585	50.2	1361.7	450.8
5	0.620	52.3	1364.3	501.5
6.	0.660	56.8	1370.3	575.0
7	0.720	58.1	1388.0	850.0
8	0.925	67.9	1401.6	1470.2

TABLE - 6.8

Mercury Recovery from Brine Sludge by Chlorination Technique

(Mercury Recovery V/s. Agitation Time)

(i) Sludge quantity taken = 1.09 Kg.
(ii) Moisture in Sludge = 69.7 %
(iii) Chlorine flow = 0.62 gms/minute
(iv) Chlorination time = 5 minutes

S. No.	Extra Agitation Time After Stopping Chlorine Flow (Minutes)	Mercury Recovery (%)	Mg (as MgO) mg/l
1	0	52.3	504.5
2	15	58.5	504.5
3	30	68.7	504.5
4	35	73.0	504.5
5	40	78.2	504.5
6	47	81.9	504.5
7	50	83.9	504.5
8	52	83.9	504.5
9	55	83.9	504.5

Run No:	Cl_2 flow (gms / mts)	Chlorination time (mts.)	% Mercury Recovery & Analysis of Chlorinated sludge filterate for Mg. afte					
			40 minutes of agitation		50 minutes of agitation		60 minutes of agitation.	
			% Hg Recovery	Mg(as MgO) (mg/l)	% Hg Recovery	Mg(as MgO) (mg/l)	%Hg Recovery	Mg(asMgO) (mg/l)
1	0.58	4	69.9	320.5	73.0	320.5	73.0	320.5
2	"	5	73.3	455.6	75.2	455.6	74.8	455.6
3	"	6	80.8	670.5	83.5	670.5	83.5	670.5
4	0.62	4	72.1	370.5	75.5	370.5	75.5	370.5
5	"	5	78.6	504.7	83.9	504.7	83.9	504.7
6	"	6	81.1	722.5	83.9	722.5	83.9	722.5
7	0.66	4	74.2	450.2	77.6	450.2	77.6	450.2
8	"	5	79.8	600.0	83.9	600.0	83.9	600.2
9	"	6	81.1	825.0	83.9	825.0	83.9	825.0

Table 6.9

Mercury Recovery from Brine Sludge by Chlorination Technique.

(i) Sludge quantity in each run = 1.09 kg. (ii) Moisture in sludge = 69.7%

Run No:	Cl_2 flow (gms / mts)	Chlorination time (mts.)	% Mercury Recovery & Analysis of Chlorinated sludge filterate fo Mg. aft					
			40 minutes of agitation		50 minutes of agitation		60 minutes of agitation.	
			% Hg Recovery	Mg(as MgO) (mg/l)	% Hg Recovery	Mg(as MgO) (mg/l)	%Hg Recovery	Mg(asMgO) (mg/l)
1	0.58	4	69.9	320.5	73.0	320.5	73.0	320.5
2	"	5	73.3	455.6	75.2	455.6	74.8	455.6
3	"	6	80.8	670.5	83.5	670.5	83.5	670.5
4	0.62	4	72.1	370.5	75.5	370.5	75.5	370.5
5	"	5	78.6	504.7	83.9	504.7	83.9	504.7
6	"	6	81.1	722.5	83.9	722.5	83.9	722.5
7	0.66	4	74.2	450.2	77.6	450.2	77.6	450.2
8	"	5	79.8	600.0	83.9	600.0	83.9	600.2
9	"	6	81.1	825.0	83.9	825.0	83.9	825.0

Table 6.10

Mercury Recovery from Brine Sludge by Chlorination Technique.

(Effect of Hg conc. in Sludge on Hg Recovery)

(i) Sludge quantity in each run = 1.09 kg.
(ii) Chlorine flow = 0.62 gm/minute
(iii) Chlorination time = 5 mintues
(iv) Agitation time = 50 minutes

Run No:	Moisture in Sludge(%)	Mercury Conc. in Sludge (mg/kg)	Mercury Recovery (%)
1	68.9	22.2	83.9
2	69.7	40.3	84.0
3	69.7	36.9	83.7
4	68.5	95.6	83.5
5	68.9	568.2	84.0
6	69.5	985.6	83.6
7	67.6	29.5	84.2

Table 6.11

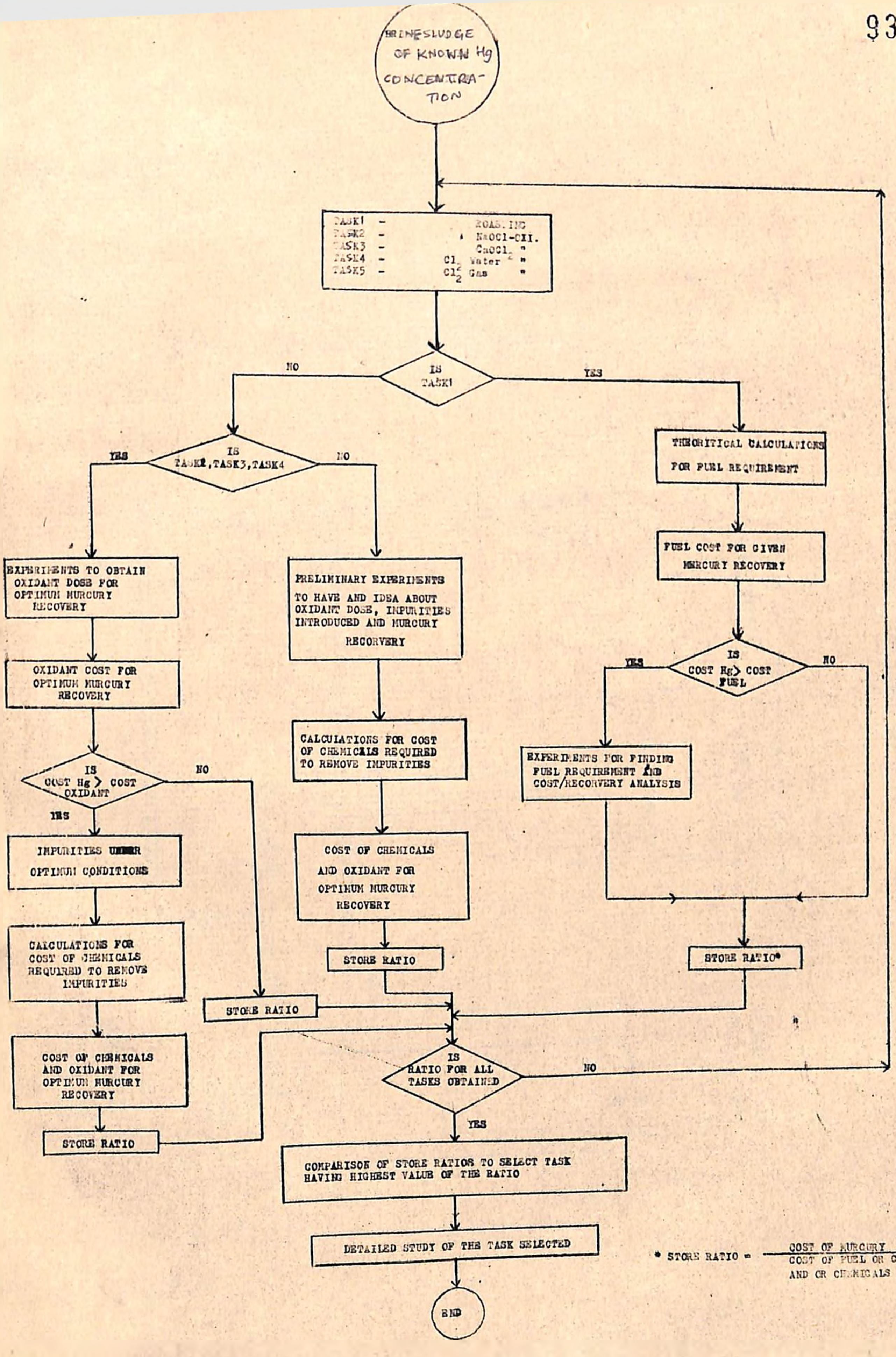
Mercury Recovery from Brine Sludge by Chlorination Technique.

(Washing of the Chlorinated sludge after filteration)

(i) Sludge quantity taken for filteration & washing in each case - 100 gms.

(ii) Moisture in sludge - 67.6%

Run No:	Quantity of Distilled water used for washing (ml)	Mercury Recovery (Percent of the total soluble Hg present in Treated sludge.)
1	0	46.6
2	30.0	76.3
3	40.0	84.5
4	45.0	89.5
5	50.0	93.5
6	55.0	95.0
7	60.0	95.0
8	70.0	95.0



* STORE RATIO = $\frac{\text{COST OF MURCURY}}{\text{COST OF FUEL OR COST OF OXIDANT AND OR CHEMICALS}}$

Fig. 6.1 EXPERIMENTAL PROGRAMME FOR MURCURY RECOVERY FROM BRINE SLUDGE

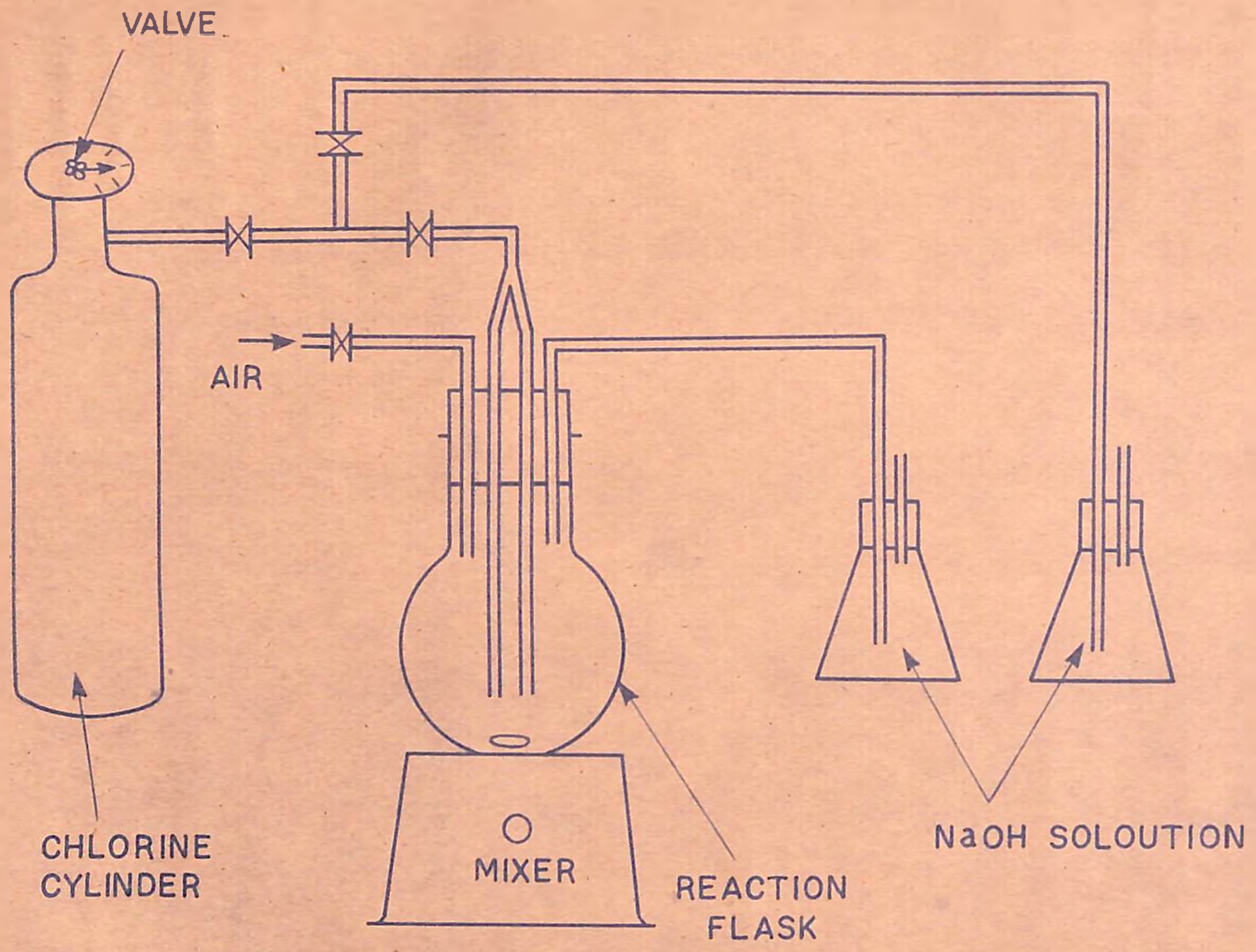


FIG. 6.2 EXPERIMENTAL SET UP FOR MERCURY RECOVERY FROM BRINE SLUDGE BY CHLORINATION TECHNIQUE

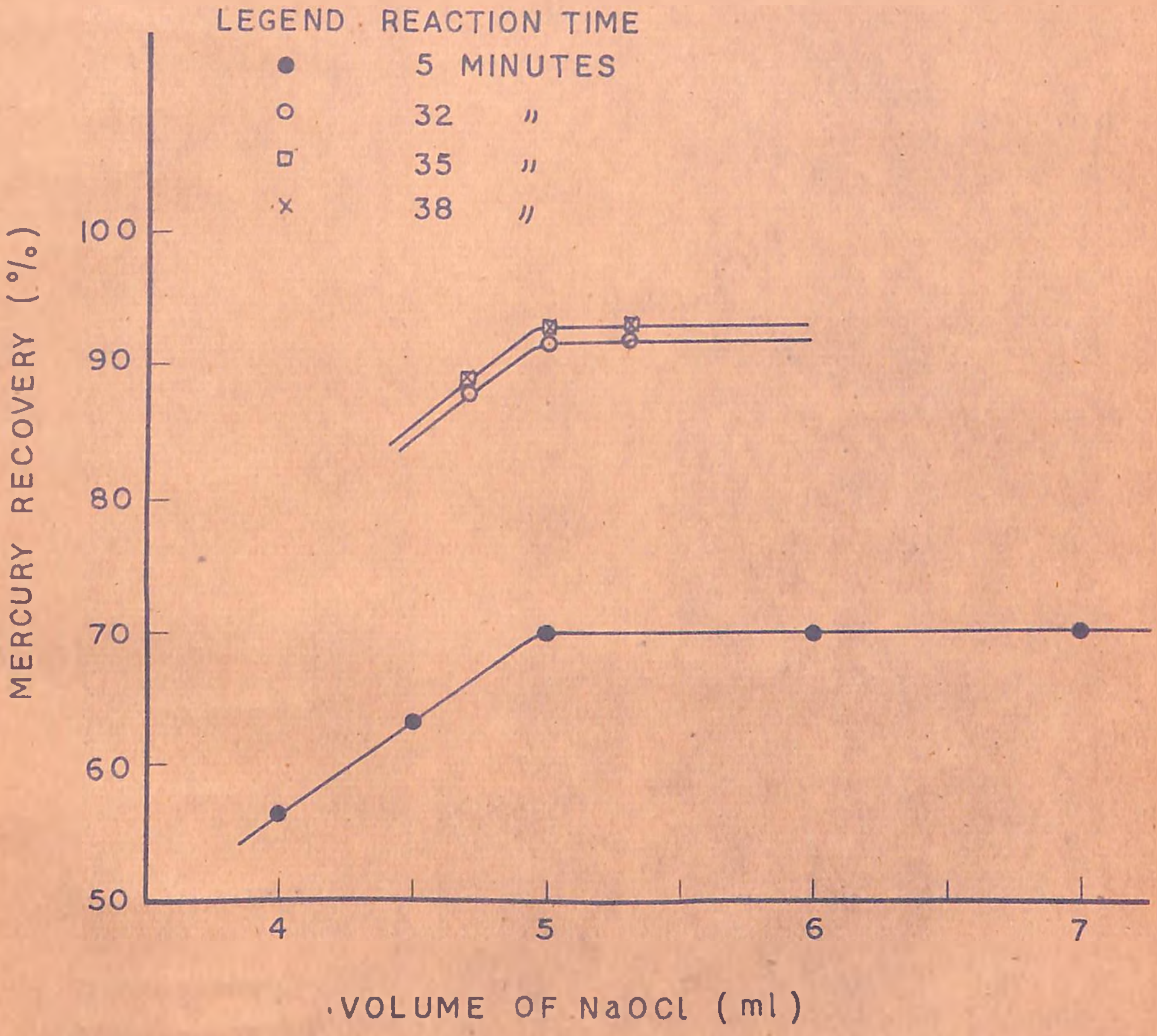


FIG. 6.3 TREATMENT OF BRINE SLUDGE WITH NaOCl (% Hg RECOVERY V/S OXIDANT QUANTITY FOR DIFFERENT REACTION TIMES).

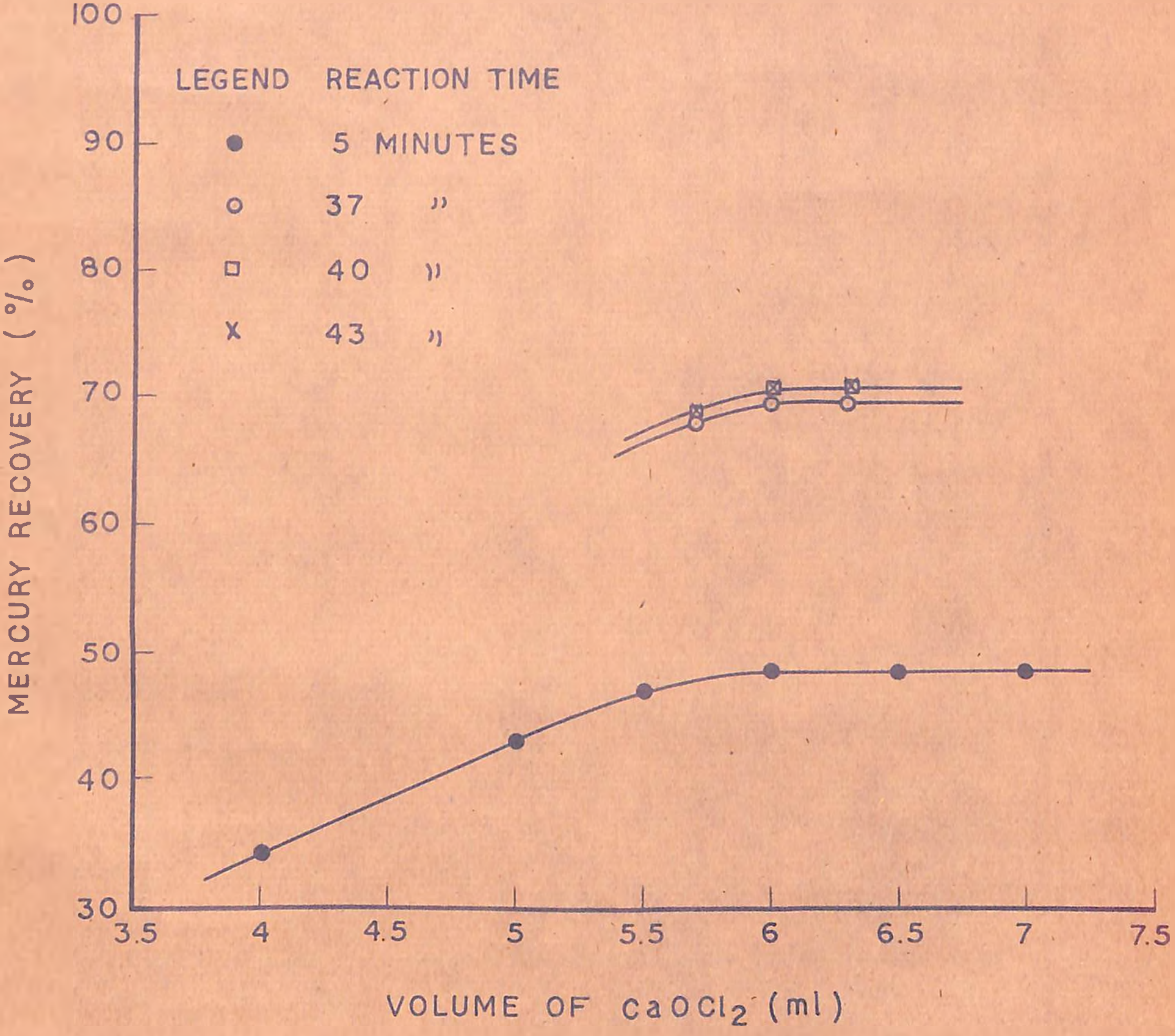


FIG. 6.4 TREATMENT OF BRINE SLUDGE $CaOCL_2$ (% Hg RECOVERY V/S SOLVENT QUANTITY FOR DIFFERENT REACTION TIMES).

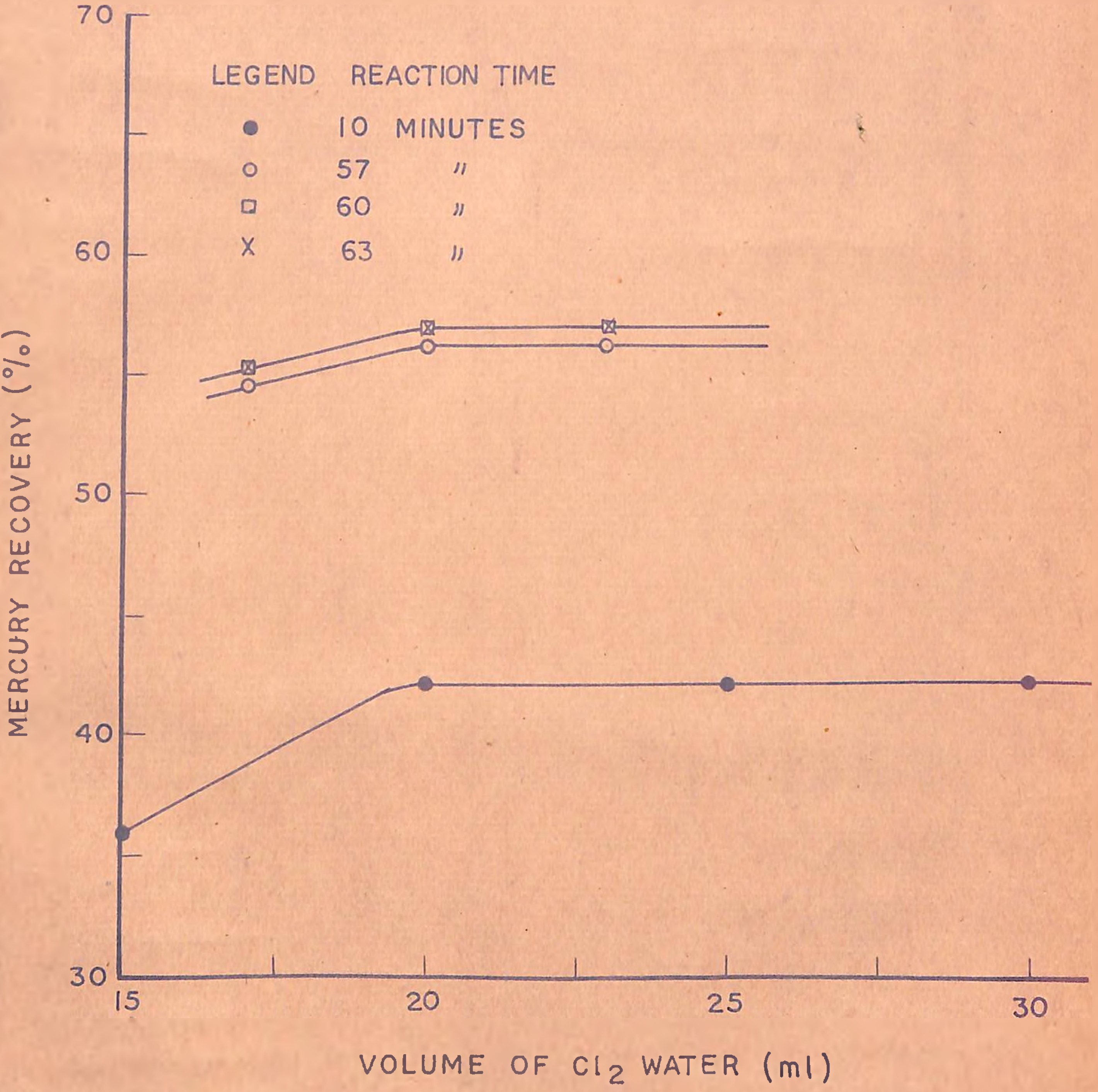


FIG. 6.5 TREATMENT OF BRINE SLUDGE WITH Cl_2 WATER (% RECOVERY V/S SOLVENT QUANTITY FOR DIFFERENT REACTION TIMES)

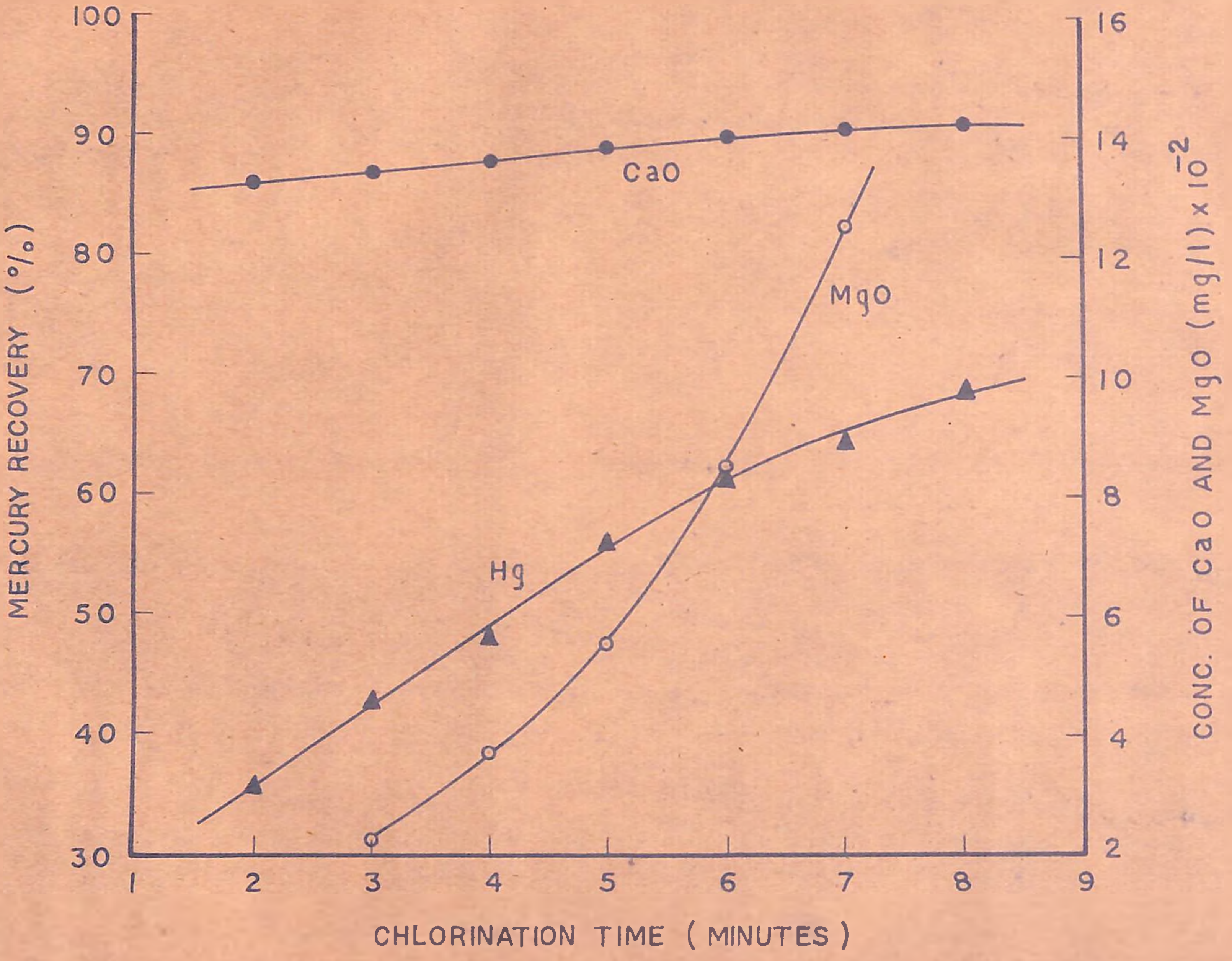


FIG. 6.6 CHLORINE TREATMENT OF BRINE SLUDGE (% Hg RECOVERY, CONC. OF Ca (AS CaO) AND Mg (AS MgO) IN THE TREATED SLUDGE FILTERATE V/S CHLORINATION TIME).

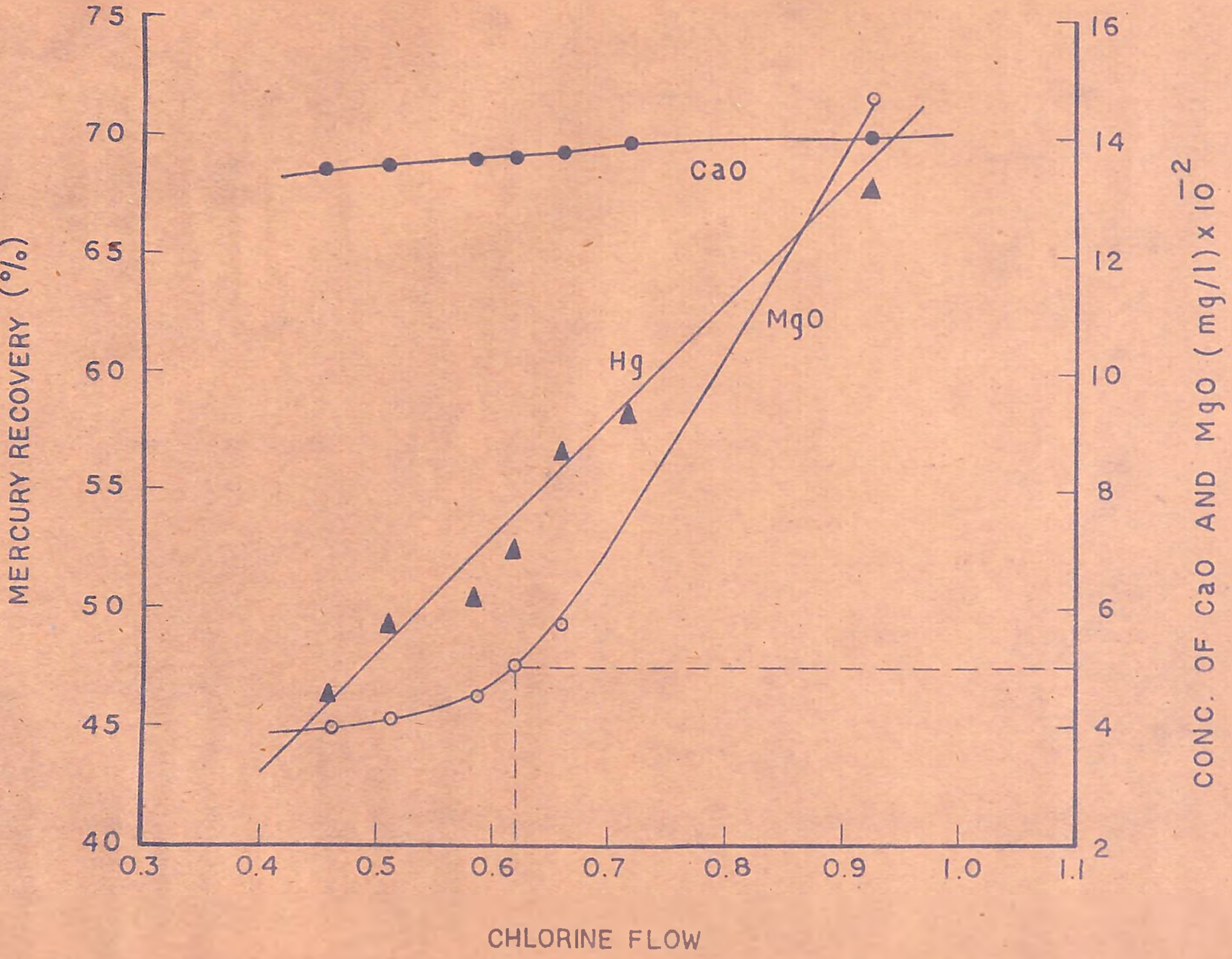


FIG. 6.7 CHLORINE TREATMENT OF BRINE SLUDGE (% Hg RECOVERY, CONCS. OF Ca (AS CaO) AND Mg (AS MgO) V/S CHLORINE FLOW).

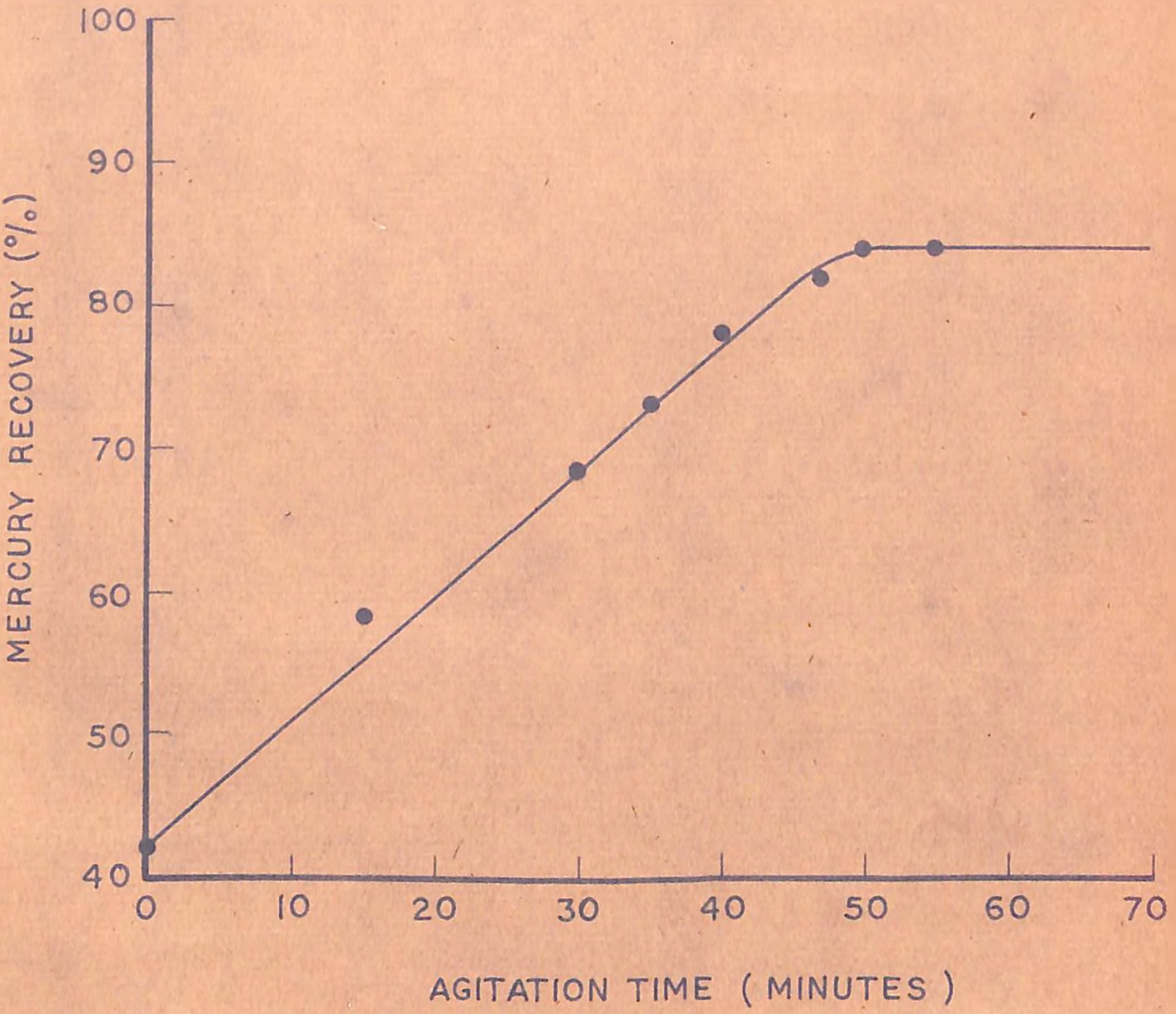


FIG. 6.8 AGITATION OF CHLORINATED SLUDGE (% Hg RECOVERY V/S AGITATION TIME).

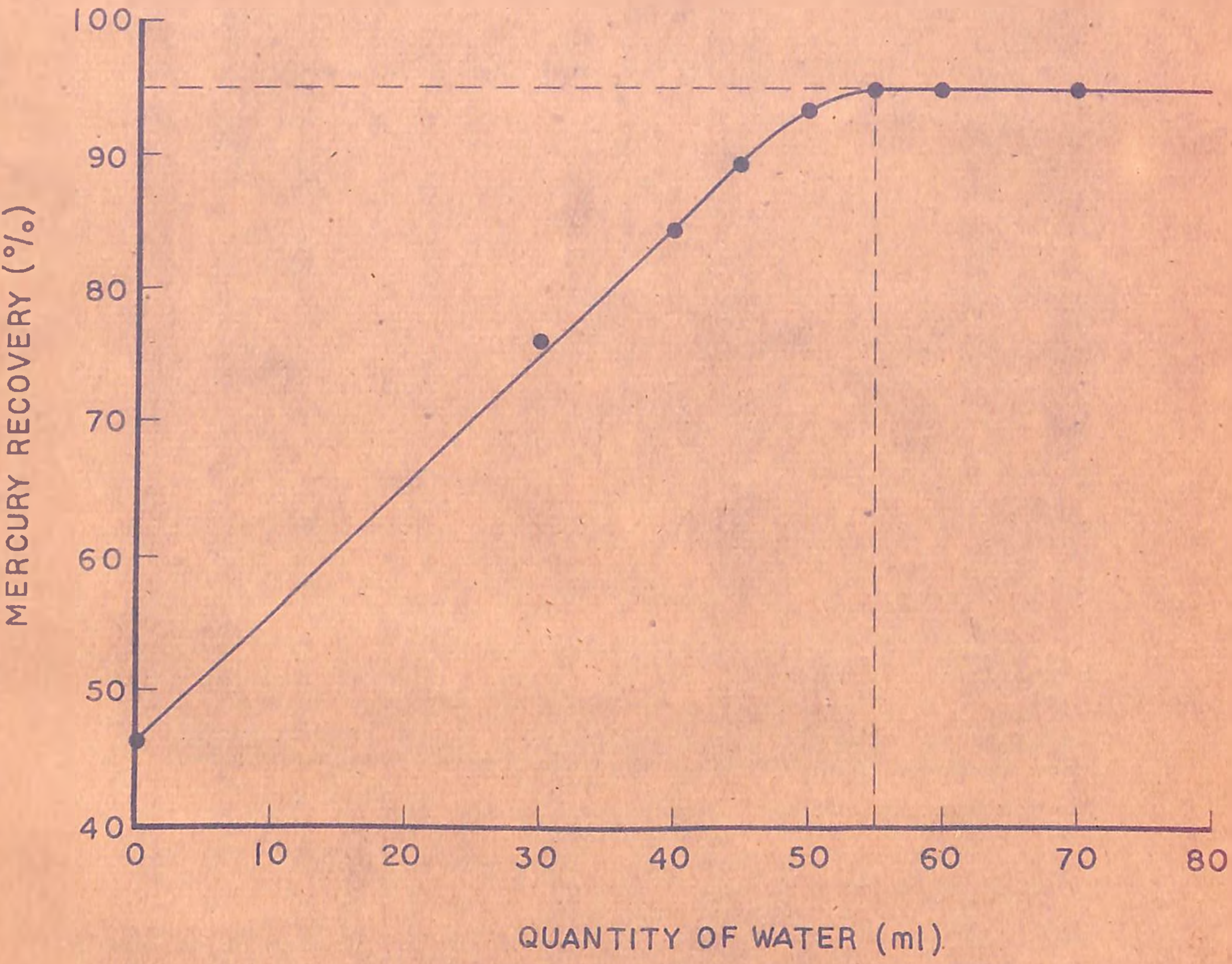


FIG. 6.9 WASHING OF THE FILTERED CHLORINATED SLUDGE.

RECYCLE OF CELL CLEANING WASTE WATER TO BRINE SYSTEM

7. RECYCLE OF CELL CLEANING WASTE WATER TO BRINE SYSTEM :

7.1 Purpose and Plan:

Although there is no regular waste water from cell house, cell cleaning operations, floor-washings, domestic water taps etc. produce waste water for short intervals of time depending upon how long these activities last. From the results of the study conducted for mercury balance of the plant it was found that more than 95% of the Hg loss in liquid stream from cell house is contributed by cell cleaning waste water alone. Hence a detailed study was conducted for finding the suitability of the recycle of this waste water to brine system. This involved :

(i) To find duration for which waste water from cell cleaning should be recycled,

(ii) Point in cell house drain system from which this waste water has to be diverted for recycle,

(iii) Quality and quantity of this waste water and their suitability for recycle to brine system, and

(iv) Point in the brine system where waste water should be recycled.

7.2 Cell House Waste Water Drain System:

Flow diagram of the system is shown in figure 7.1. Waste Water resulting from cell cleanings first goes to a mercury trap to retain any metallic mercury carried from the cell under cleaning / maintenance. Over flow from this trap goes to open channels where waste water from water taps, floor washings etc. flows into these channels. These channels lead to a set of four troughs kept in series so that the over flow from one goes to the next and so on before it is discarded as liquid waste after fourth trough. The use of these troughs is to retain any metallic mercury carried by the waste water from the cell house floor.

7.3 Duration of Recycle:

To find the time for which the recycle of the waste water should be continued, results of thestudy conducted under section 5·3(2)A(ii) for mercury loss estimation in this stream, were analysed. It was found that the concentration of mercury in this waste water reduces to practically zero after 50 minutes from the start of a cell cleaning operation. It was therefore concluded that waste water resulting during first 50 minutes of a cell cleaning operation should be studied for its recycle to brine system.

7.4 Selection of Diversion Point:

In selecting a point in the cell house drain system from where the waste water from cell cleanings should be recycled, the criterianadopted was ~~that~~ the minimum recycle volume and maximum use of the existing mercury recovery troughs.

There are two points in the drain system from where waste water can be diverted to brine system. These are inlet to the trough (or overflow from mercury trap

(point'C' in fig. 7.1) and out let from the troughs (point 'D').

To check whether metallic mercury is carried by the waste water inspite of the mercury trap, samples of this waste water were collected from inlet and out let of the troughs during a cell cleaning and analysed for their respective Hg concs. This analysis was done in both the situation of the troughs namely, when they were clean and when they contained Hg collected as a result of floor washings. Results are given in table 7.1 and also in fig. 7.2.

Following observations could be made from these data.

(a) When troughs were clean the conc. of mercury in the inlet and outlet stream remains the same. This means that the overflow from mercury trap does not contain any settlable mercury.

(b) When the troughs contained Hg bearing sludge, conc. of Hg in the outlet from the troughs was found to be more than that in the inlet stream. This could be due to carry over of Hg settled in the troughs. It is therefore clear that as far as waste water from cell cleanings is concerned, troughs in the drain system have no significance and this waste water can be diverted without sending to these troughs.

As described in the preceding sections waste water from cells after passing through the mercury trap goes to open channels, troughs etc. Waste water from other activities in the cell house, if going on at the time of cell cleaning is also likely to join waste water from cell cleanings and increase the volume to be recycled to brine system. Moreover the over flow of the Hg trap is about 6 to 7 feet high from the ground so the advantage of gravity flow can also be taken if required for recycling the waste water. It is therefore desired that over flow ffom mercury trap should be diverted to brine system.

7.5 Quality of the Waste Water :

To ckeck whether the impurities which are likely to be present in the cell cleaning waste water are within the tolerable limits in the brine system, a composite sample of this waste water was made by collecting equal volumes of the same from Hg trap overflow after every two minutes during a cell cleaning. Sampling was continued till the waste water became visibly clear (Indication of very low Hg conc. observed during Hg loss assess-ment studies). Composite samples thus obtained were analysed. Results are given in table 7.2. On compa-ring these results with the avg. analysis of the brine, it was found that the concentration of iron in the cell cleaning waste water is high enough to disturb the brine quality. However this iron is expected to get precipitated as $Fe(OH)_3$ in purifiers (brine house) where the medium is alkaline. To varify this following experiment was conducted:

Composite sample of the cell cleaning waste water was mixed with brine collected from purifiers in the ratio 10:240 (The maximum flow encountered during cell cleaning was 5 M^3 / hr. which on giving 100% margin comes to 10 M^3/hr and 240 M^3/hr being the brine flow through purifiers). Mixture was then filtered and filterate was analysed for its iron conc., and it was found that iron reduces to non detectable levels in this filterate.

Since recycle of the waste water to purifiers is equivalent to recycle to sludge pits in brine section (because any brine recovered from this sludge is recycled to purifiers),it was decided to recycle waste water to sludge pits to make use of the gravity flow.

Table 7.1

Analysis of Troughs (in Cell House Drain System) Inlet and Out let Waste Water Stream During Cell Cle

Time of Sample collection from start of cell cleaning (Minutes)	Analysis of troughs inlet&outlet streams									
	When troughs are clean					Troughs contain Hg bearing sludge.				
	WW* flow (M^3/hr)	Hg conc. Inlet (gms/M^3)	Hg entering troughs (gms/hr)	Hg conc. outlet (gms/M^3)	Hg leaving the troughs (gms./hr)	WW* flow (M^3/hr)	Hg conc. Inlet (gms/M^3)	Hg entering troughs (gms./hr)	Hg conc. outlet (gms/M^3)	Mercury leaving troughs (gms/hr).
0	8.5	21.5	182.8	21.5	182.6	5.4	11.5	62.1	31.5	170.1
15	8.5	29.6	251.6	29.6	251.6	5.4	26.3	142.0	46.4	250.6
20	3.8	286.0	1086.8	286.0	1086.8	7.3	165.0	1204.5	218.9	1598.0
25	"	-	-	-	-	7.3	162.5	1186.3	215.6	1573.9
30	3.8	282.5	1073.5	282.5	1073.5	7.3	160.8	1173.8	214.2	1563.7
35	3.6	17.5	63.0	17.5	63.0	5.2	3.5	18.2	13.9	72.3
40	3.6	1.8	6.5	1.8	6.5	3.2	2.0	6.4	2.1	6.7
50	3.6	1.7	6.1	1.7	6.1	3.2	2.0	6.4	2.0	6.4

* Waste Water.

Table 7.2

Quality of cell cleaning Waste Water with respective impurities present.

Sampling No:	Analysis of the composite sample of cell cleaning Waste Water									
	Temp. °C	pH	Free Cl_2 (mg/l)	TSS* (gpl)	Ca (as CaO) (mg/l)	Mg(as MgO) (mg/l)	SO_4^{--} (gpl)	ClO_3^- (as $NaClO_3$) (gpl)	Cl^- (as NaCl) (gpl)	Iron (mg/l)
1	51.0	7.0	Nd**	2.14	539	20	4.39	2.39	168	110
2	50.5	7.0	"	2.05	490	18	4.02	2.19	154	120
3	53.4	7.0	"	2.29	635	24	5.22	2.85	200	30
4	52.0	7.0	"	2.22	560	21	4.58	2.50	176	50
5	53.5	7.0	"	2.32	650	25	5.33	2.91	205	50
6	53.4	7.0	"	2.30	637	24	5.23	2.88	201	65
7	53.0	7.0	"	2.25	622	24	5.10	2.78	196	40
8	53.5	7.0	"	2.28	654	25	5.33	2.90	206	50
9	54.5	7.5	"	2.40	725	26	5.98	3.25	229	60
10	53.5	8.0	"	2.28	646	25	5.34	2.92	204	150

* Total suspended solids.

** Not detectable.

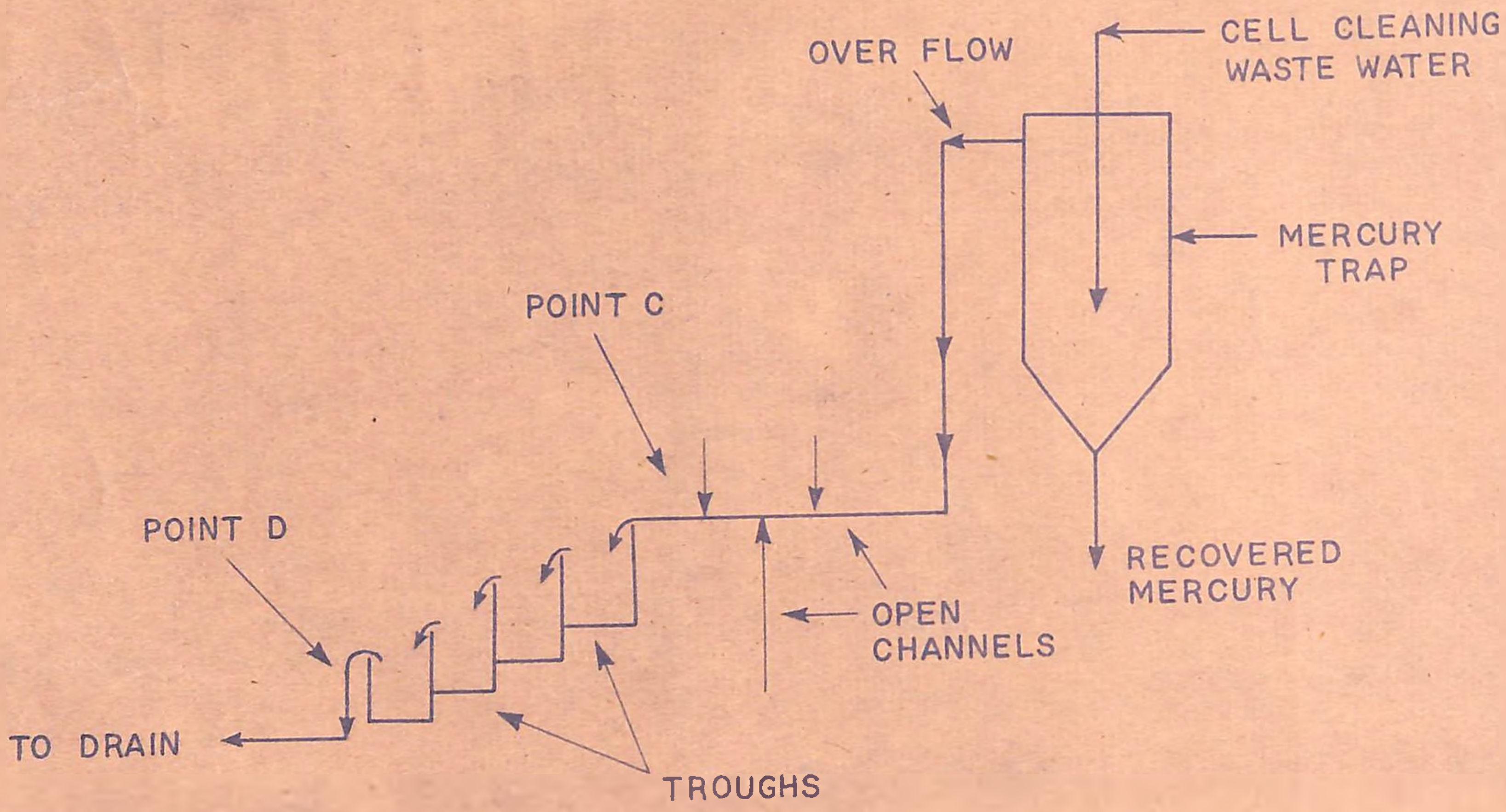


FIG. 7.1 , CELL HOUSE DRAIN SYSTEM

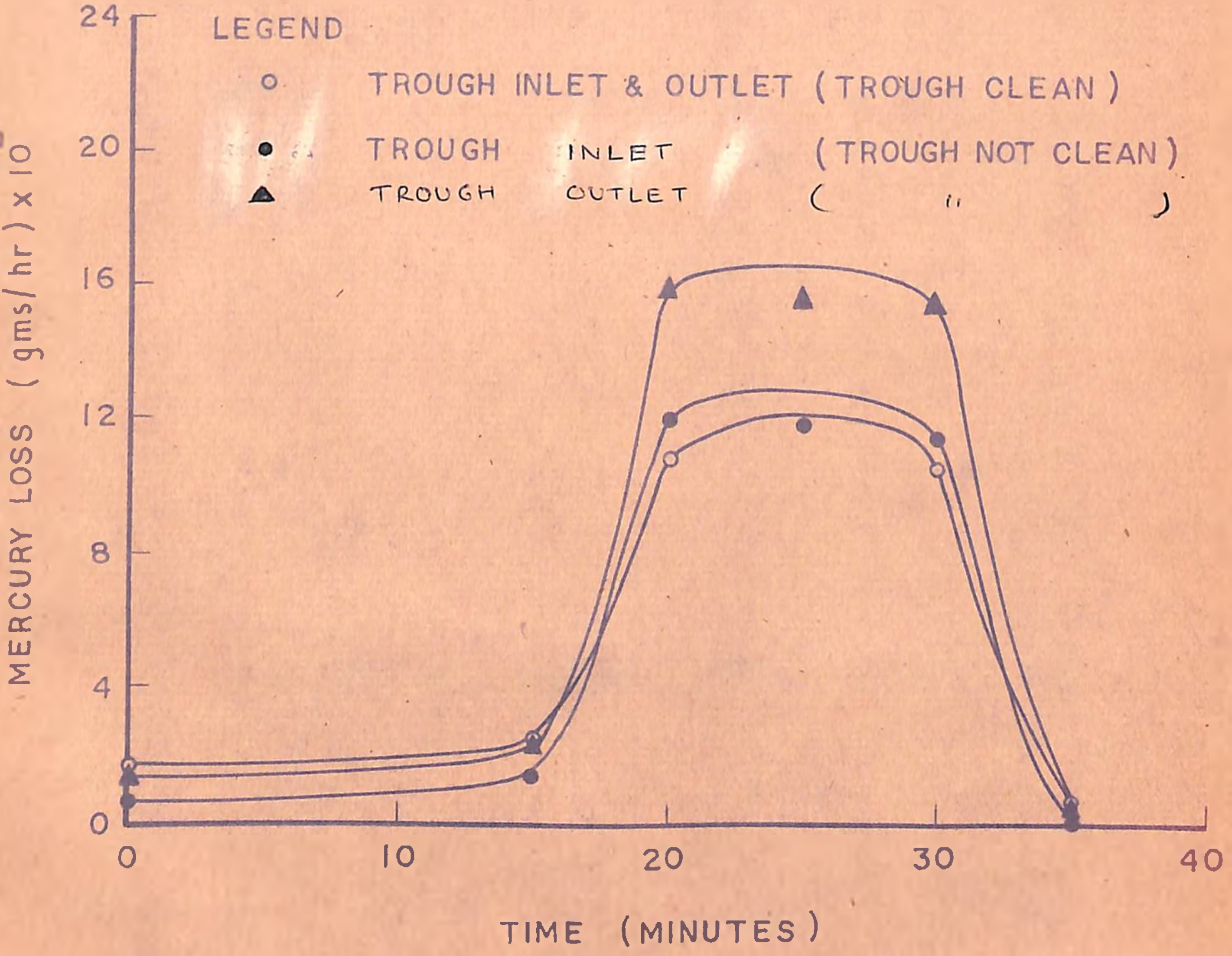


FIG. 7.2 CELL CLEANING WASTE WATER ANALYSIS (Hg LOSS V/S TIME).

MERCURY RECOVERY FROM HYDROGEN GAS

8. MERCURY RECOVERY FROM HYDROGEN GAS :

8.1 Selection of Technique:

Although recovery of mercury from Hydrogen gas is not economic, however, this is likely to improve the quality of hydrochloric acid obtained from hydrogen gas and therefore the selling price. Besides this, removal of Hg from hydrogen gas eliminates all subsequent contaminations like waste water etc. in HCl plant. Since quality of the product HCl is given emphasis, the criterian fixed for selecting a technique for this purpose was the purity of hydrogen.

Out of the two techniques namely scrubbing with NaOCl and activated charcoal adsorption reported, the latter is more efficient.

Detailed experiments were conducted with activated carbon, received from Narbada Valley Corp., Gujrat for optimizing parameters involved, studing the effect of moisture in hydrogen gas on mercury adsorption, determination of Hg adsorption capacity of carbon bed and break through curve study.

8.2 Activated carbon Adsorption Techinque:

8.2.1 Parameters:

Following parameters are likely to have an influence on the service time of an adsorption bed:

(i) Grain size of the activated carbon.

(ii) Bed Size (Length/Diameter = ratio)

(iii) Gas flowrate

(iv) Bed temperature

(v) Conc. of Hg in the feed stream

(vi) Conc. of other constituents which can also be adsorbed.

In the present case the temperature of the hydrogen gas and conc. of Hg in the gas remains nearly constant, therefore their affect on the bed service time was not studied. Regarding the rise in temprature of the bed as a result of adsorption (being an exothermic phenomenon) results of the preliminary experiments showed no detectable rise in temperature of the bed and this factor was also ommitted for experimental programme.

Species present in Hydrogen gas, other than mercury was moisture and experiments were therefore designed to first find optimum values of hydrogen flow, bed size (L/D) and grain size and then study the effect of moisture on the service time (or adsorption capacity of carbon) of the bed.

8.2.2 Experimental setup:

Set up used for the purpose shown in fig. 8.1. Hydrogen gas was taken directly from the supply line to HCl plant.

A calibrated orificemeter was used to measure the flow of hydrogen gas. The calibration curve is shown in fig. 8.2. Arrangements were also made to measure the temperature and pressure of the orifice inlet gas to make necessary temperature and pressure corrections to the measured flows. However there was a negligible variation in both of these quantities throughout the experiments.

Details of these alongwith the method of orifice calibration followed is given in appendix 8.1.

A glass column was used. Arrangements were also made to measure the pressure drop across the bed.

8.2.3 <u>Procedure</u>:

(i) For measuring Hg content in feed gas, hydrogen gas was passed directly through acidified $KMnO_4$ by passing the bed, at a known flow for a known time. The resulting solution was then analysed for its total Hg content. Conc. of mercury in hydrogen gas was then calculated from the quantity of the gas sampled and quantity of Hg obtained by analysis. This was repeated each time when any adsorption experiment was started (It was found that the conc. of Hg in hydrogen gas, however varied to the extent of ± 2.5% of the average only).

(ii) 100 gms of the activated carbon was packed in the glass column of known diameter. Bulk density was found to be 0.57 kg / litre.

Mercury bearing hydrogen gas was allowed to be sucked inside the activated carbon bed with the help of a vacuum pump.

The gas emerging from the adsorption column was allowed to bubble continuously through acidified $KMnO_4$ solution kept in line and then to the orifice meter through a control valve. Acidified $KMnO_4$ solution was replaced from time to time with fresh $KMnO_4$ solution and each time the solution removed was analysed for its Hg conc. For a particular set of conditions this was continued till Hg was detected in the gas emerging from the bed.

Initially a 2^3 set of factorial experiments were conducted corresponding to two levels of each of the three parameters studied (namely L/D ratio of packing, Grain size and hydrogen flow). From the results obtained in these '8' experiments the favourable directions i.e. the lowest possible L/D ratio, proper grain size and maximum hydrogen flow were obtained.

Further experiments were then conducted to find optimum parameters. Repeat runs were made so as to cover both the flow conditions corresponding to different combinations of particle size and L/D ratio and maximum repeat runs were made near optimum values.

8.2.4 Results and Discussion :

Results are given in table 8.1. It can be seen from these results that corresponding to same quantity of activated carbon, grain size and hydrogen flow the adsorption capacity of the activated carbon remains the same for a decrease in L/D ratio upto 2.44. L/D ratio of 2.44 was therefore selected because higher L/D would result high pressure drop.

There was a decrease in the adsorption capacity of the bed in going from a mesh size of 4/16 to 4/6. This is because of the fact that greater the grain size less is the effective surface area. On the other hand going from 4/16 to 6/16 (4/16 > 6/16) mesh the adsorption capacity should have shown an increase but in our result there was no increase observed which may be because of the fact the average particle size in cases of 4/16 and 6/16 might be appox. the same. Therefore grain size of 4/16 mesh was finalized.

Coming to hydrogen flow, all the other conditions remaining the same it was found that the adsorption capacity of the carbon remains the same for an increase in flow of hydrogen upto 26.8 liters/hr. After this the capacity starts decreasing. This again can be explained by the fact that for a flow of 26.8 litres / hr and less enough contact time is provided for Hg to be adsorbed on activated carbon. Hence corresponding to 100 gms. of activated carbon, the desired values of the parameters involved thus obtained are

L/D = 2.44
Grain size = 4/16 mesh
Hydrogen flow = 26.8 liters / hr.

8.2.5 Effect of Moisture on Hg Adsorption:

8.2.5.1 Experiment:

The experimental arrangements for this purpose was same as described before except for a sulphuric Acid bubbler to remove moisture from the feed stream. For studying the nature of the break through curve, analysis of the Hydrogen gas was continued even after mercury started coming in the exist gas. The time when mercury is detected in this outlet gas is know as the 'break point' and the variation of Hg conc. in the exist gas with time after this point is known as 'Break through Curve'. Repeat runs were also made to check the reproducibility. From hydrogen flow, time, quantity of conc. H_2SO_4 taken for drying and dilution of acid during the experiment, the conc. of moisture in hydrogen was calculated.

8.2.5.2 Result and Discussions:

Results of the experiment conducted for break through curve ' are given in table 8.2 and shown in fig 8.3 Conc. of moisture in hydrogen and Hg in H_2SO_4 as referred in the preceding section were found to be 14.58 gms/m^3 and 3.2 ppm . Since all the further experiments for adsorption study were conducted with dry hydrogen, H_2SO_4 was analysed from time to time and it was found that on an avg. about 14.5 gms. of moisture is contained in 1m^3 of hydrogen and avg. Hg conc. in H_2SO_4 was found to be 3.5 ppm.

Now comparing results given in table 8.2 and 8.1, it can be seen that under similar conditions of L/D , particle size and flow the volume of hydrogen treated by the same quantity of carbon is more than doubled, if hydrogen is dried before it is sent to the adsorption column . This indicates that a part of the active sites on the activated carbon are occupied by moisture thereby reducing its capacity to adsorb Hg. The details of the mechanism were not studied because it was outside the scope of this work .

The shape of the break through curve obtained (refer fig. 8.3) was quite shallow, i.e. increase in Hg conc. in the hydrogen gas emerging from the adsorption column is very gradual, indicating that even at break point a significant portion of the adsorption bed still remains unused. It is suggested that for such a system , use of two or more adsorption columns in series should be made to utilize the adsorption capacity of activated carbon to a maximum extent. Further experiments were therefore conducted with two adsorption columns in series and with dry hydrogen gas.

8.2.6 (i) <u>Sulfuric Acid Requirement</u>:

Volume of hydrogen produced / day at 721.5mm pressure and 26.5°C (obtained from stoichiometric calculations) = 38856 M^3.

Moisture in hydrogen = 14.5 gms / M^3

Total moisture to be removed per day =

$$= 14.5 \times 38856 \times 10^{-3} \text{ Kgs}$$

$$= 563.4 \text{ kgs}$$

let 'x' kg per day of 98% H_2SO_4 is required to remove this moisture. Also it was found from consultation with plant personnel that the conc. of H_2SO_4 should not be allowed to go below 70% for an effective drying.

From Acid Balance

$$'x' \times 0.98 = ('x' + 563.4) \times 0.70$$

hence 'x' = 1408.5 Kg

= 1.4 tones / day approx.

It is important to mention here that diluted acid is re-useable in the plant somewhere else.

(ii) <u>Adsorption Capacity</u>:

Quantity of carbon = 100 gms.

Avg. Hg conc. in hydrogen = 22.5 µg/l.

Volume of hydrogen from which Hg is removed to non detectable by 100 gms of carbon = 26.8×62 = 1661.6 liters (Ref table 8.2).

Therefore adsorption capacity of carbon = 22.5 × 1661.6 μg/100gm of activated carbon = 0.374 gms of Hg/Kg of activated carbon.

8.2.7 Experiments with two Beds in Series:

(i) Experiments Conducted:

Keeping the quantity of activated carbon same and equal to 100 gms three stage cascade experiments using three beds were conducted in such a way that when two beds were in adsorption cycle the third was being regenerated. A hydrogen flow of 26.8 liters / hr and L/D ratio of 2.44 for each bed was maintained.

These cascade experiments involved introduction of a new bed down stream and each time a completely spent bed up stream was removed from service for regeneration. The sequence of operation is shown in fig. 8.4.

In any one step the No: 1 adsorber in line was the partially saturated one which was No:2 in the preceding step, while the 2nd adsorber was being regenerated. These experiments were conducted for two complete cycles.

(ii) Results & Discussion:

Results of these experiments are given in table 8.3.

From these results it is clear that every bed will be in adsorption cycle for about 150 hrs before it is removed for regeneration. For the first 75 hrs it will be first adsorber among two in series and for rest of 75 hrs it will be second, and after each 75 hrs one adsorber has to be taken out for regeneration.

8.3. Desorption Studies of the Spent Bed For Regeneration of the Bed:

8.3.1 Eluting agent:

Steam and hot air are the most common eluting agents reported in literature for regenerating the spent bed and to recover the adsorbate. In case of the steam the bed requires drying with hot air after regeneration. Moreover in the present case of recovering Hg from spent activated carbon, some mercury is likely to be carried in the condensate water. This is likely to creat water pollution problems. It was therefore decided to elute the spent bed with hot air.

8.3.2 Experimental:

Experimental set up used for this purpose has been shown in fig. 8.5. Air was taken from the compressed air line provided in the lab. A welding torch (commonly familiar as PVC Welding torch) was used to heat the air.

For control of air flow, a valve was provided before the inlet to the PVC torch. Flow was measured down stream the bed with the help of a precalibrated orifice meter (Calibration curve is showin in fig. 8.6). Arrangements were made to measure the temperature and pressure of the gas at inlet to orifice meter.

A thin capillary was inserted at the bed axis such that a sliding thermometer can measure bed temperature at any point. The temperature was varied by varying the temperature of the hot air with the help of a regulator connected to the electrical heater of the torch.

8.3.3 Procedure:

Hot air was purged into the spent bed and the emerging gas with recovered mercury was passed through a series of two gas wash bottles(bubblers) containing acidified $KMnO_4$ solution to dissolve Hg carried by hot air. After the $KMnO_4$ solution the gas was finally vented to atmosphere through orifice meter.

Gas wash bottles containing $KMnO_4$ were removed from time to time and each time they were replaced by similar bottles containing fresh acidified $KMnO_4$ solution. The solution removed was analysed for its total Hg content. This was continued till

Hg conc. in the air emerging from the bed reduced to non-detectable levels. For finding the optimum values of bed temperature and air flow a 2^2 factorial experiments were conducted. The temperature refered here indicates the temperature measured at the centre of the bed and the flow of air at conditions of pressure and temperature as 715mm of Hg and 25.5°C. Repeat runs were also made near optimum values.

Based on the results of these experiments further experiments were conducted to obtain optimum values of parameters.

8.3.4 Results and Discussion:

Results are given in table 8.4.

From these results it can be seen that corresponding to bed temperatures of 100 and 110°C both flows of air (viz 211.2 and 253.4 liters/hr) gives the same recovery of about 96.4% in 18 hrs time. Also in all these cases Hg in the emerging gas goes down to undetectable levels (i.e. almost complete regeneration) in about 46-47hrs. Corresponding to same temperature of 100°C and time as 18 hrs, the recovery decreases as the air flow is reduced below 211.2 literes per hr. It can also be seen that corresponding to same flow and time the percentage Hg recovery again decreases as temperature is reduced below 100°C. The optimum values of these two parameters therefore selected are 100°C and 211.2 liters/hr for 100 gms of activated carbon taken for regeneration. The shape of the desorption curve (which remains same) for both the temperatures 100 as well as 110°C irrespective of flow being 211.2 or 253.4 liters/hr is shown in fig.8.7. It can be concluded from these curves that regeneration should be done only for 18 hrs. About 96.4% Hg will be recovered in thisperiod and remaining Hg should be left in the carbon adsorbed permanently,as it takes a lot of time for recovery.

8.3.5 Reuse of the Regenerated Carbon:

To check whether regeneration reduces the adsorption capacity of the activated carbon, each time the bed was regenerated it was again taken for a fresh adsorption cycle. This regeneration and reuse of the same bed was done four times. Results indicated that there was no detectable decrease in the adsorption capacity of the activated carbon as a result of regeneration with hot air. These also indicated that for the bed regenerated for only 18 hrs and used for adsorption all the Hg adsorbed this time will be recovered in 18 hrs only in 2nd regeneration.

Appendix 8.1

Orifice Calibration

I. Experimental set-up is shown in fig. 8.8.

A gas flowmeter was used as standard.

II. Procedure:

Gas for which the orifice was to be calibrated (i.e. hydrogen or air) was allowed to pass through the orifice into the gas flowmeter. Corresponding to a particular 'Δp' across the orifice, flow of the gas was measured. By changing flow with the help of the control valve (refer fig. 8.8) flows for different 'Δp' values were obtained.

III. Calibration Curve:

For a given orifice, the flow of the fluid flowing through it is directly proportional to the square-root of the pressure drop across the orifice[20].

i.e. flow

To obtain a calibration curve therefore '$\sqrt{\Delta p}$' values were plotted against flows. Two orifices used in the present study were calibrated in this way. One of lower range for hydrogen and other of higher range for air. Calibration curves corresponding to these have been shown in figures 8.2 and 8.6 respectively.

Table 8.1

Mercury Removal from Hydrogen gas by Activated Carbon

(Optimization of L/D, particle size & flow)

Run No:	Packing L/D	Pressure drop across the bed (mm of water)	Grain size of Carbon (Mesh)	H_2 flow (litres/hr)	Volume of H_2 treated*by 100 gm of activated carbon
1	2	3	4	5	6
2	8.23	6	4/16	25.04	776
3	"	"	"	"	780
1	"	"	"	29.76	689
6	"	"	4/6	25.04	701
4	"	"	"	29.76	565
5	"	"	"	"	562
9	3.48	3	4/16	25.04	779
7	"	"	"	29.76	684
8	"	"	"	"	684
11	"	"	4/6	25.04	705
12	"	"	"	"	708
10	"	"	"	29.76	569
26	2.44	2-3	6/16	25.04	775
27	"	"	"	"	780
24	"	"	"	29.76	685
25	"	"	"	"	685
28	"	"	4/16	23.57	778
20	"	"	"	25.04	780
29	"	<2	"	26.80	777
30	"	"	"	"	780

1	2	3	4	5	6
31	"	"	"	27.99	699
32	"	"	"	"	700
19	"	"	"	29.76	684
23	2.13	"	"	25.04	726
21	"	"	"	29.76	595
22	"	"	"	"	590
15	1.78	1	"	25.04	601
13	"	"	"	29.76	535
14	"	"	"	"	540
18	"	"	4/6	25.04	576
16	"	"	"	29.76	446
17	"	"	"	"	450

* Refers to volume of hydrogen obtained with no detectable Hg.

Table 8.2

Mercury Removal from Hydrogen gas by Adsoprtion on Activated Carbon.

S.No:	Time of sample collection from the start of Expt.(hrs).	Hg conc. in the hydrogen gas emerging from bed (μg / 1)	
		Run 1	Run 2
1	60	Not Detectable	Not Detectable
2	61	"	"
3	62	"	"
4	63	0.26	0.25
5	64	0.37	0.37
6	65	0.75	0.72
7	69	1.68	1.65
8	71	2.43	2.43
9	74	5.22	5.24
10	75	9.33	9.35
11	76	13.10	13.13
12	77	16.80	16.90
13	78	22.30	22.30
14	79	22.30	22.30
15	80	22.30	22.30

Table 8.3

Mercury Adsorption on Activated Corbon. (Three stage Cascade Experiments with two adsorption beds in series.)

Hydrogen Flow rate in each experiments = 26.8 liters/hr.

S.No:	First Adsorber in line.	Second Adsorber in line	Adsorber in Regeneration	Qty. of Hg free H_2 obtained	
				Time for which No Hg detected in H_2 (hrs.)	Total volume of H_2 treated (litres).
1	C	A	B	75.5	2023.4
2	A	B	C	75.0	2010.0
3	B	C	A	75.0	2010.0
4	C	A	B	75.0	2010.0
5	A	B	C	75.5	2023.4
6	B	C	A	75.0	2010.0
7	C	A	B	75.0	2010.0

Table 8.4

Regeneration of Spent Carbon with Hot Air

Run No:	Temp. of bed Measured at the centre along the axis (°C)	Air Flow Across the Orifice (Lit./Hr.)	Temp. of Orifice Inlet Air (°C)	Mercury Recovery				Time Require for 100% Hg Recovery.
				Time Hrs.	% Hg Recovery	Time Hrs.	% Hg Recovery	
3	110	253.4	25.5	18	96.50	-	-	46
1	110	211.2	26.0	18	96.42	-	-	46
2	110	211.2	26.0	18	96.48	-	-	47
4	100	253.4	25.8	18	96.38	-	-	46
5	100	253.4	25.8	18	96.45	-	-	47
6	100	211.2	26.2	18	96.40	-	-	46
7	100	211.2	26.2	18	96.45	-	-	46
14	100	190.1	25.0	18	83.15	24	96.45	53
15	100	190.1	25.0	18	83.20	24	96.40	53
13	100	169.0	25.8	18	57.52	33	96.39	70
11	95	211.2	26.0	18	78.50	26	96.35	55
12	95	211.2	26.0	18	78.45	26	96.40	55
8	90	253.4	25.3	18	68.50	28	96.43	58
9	90	211.2	25.0	18	61.60	30	96.42	61
10	90	211.2	25.0	18	61.54	30	96.40	61

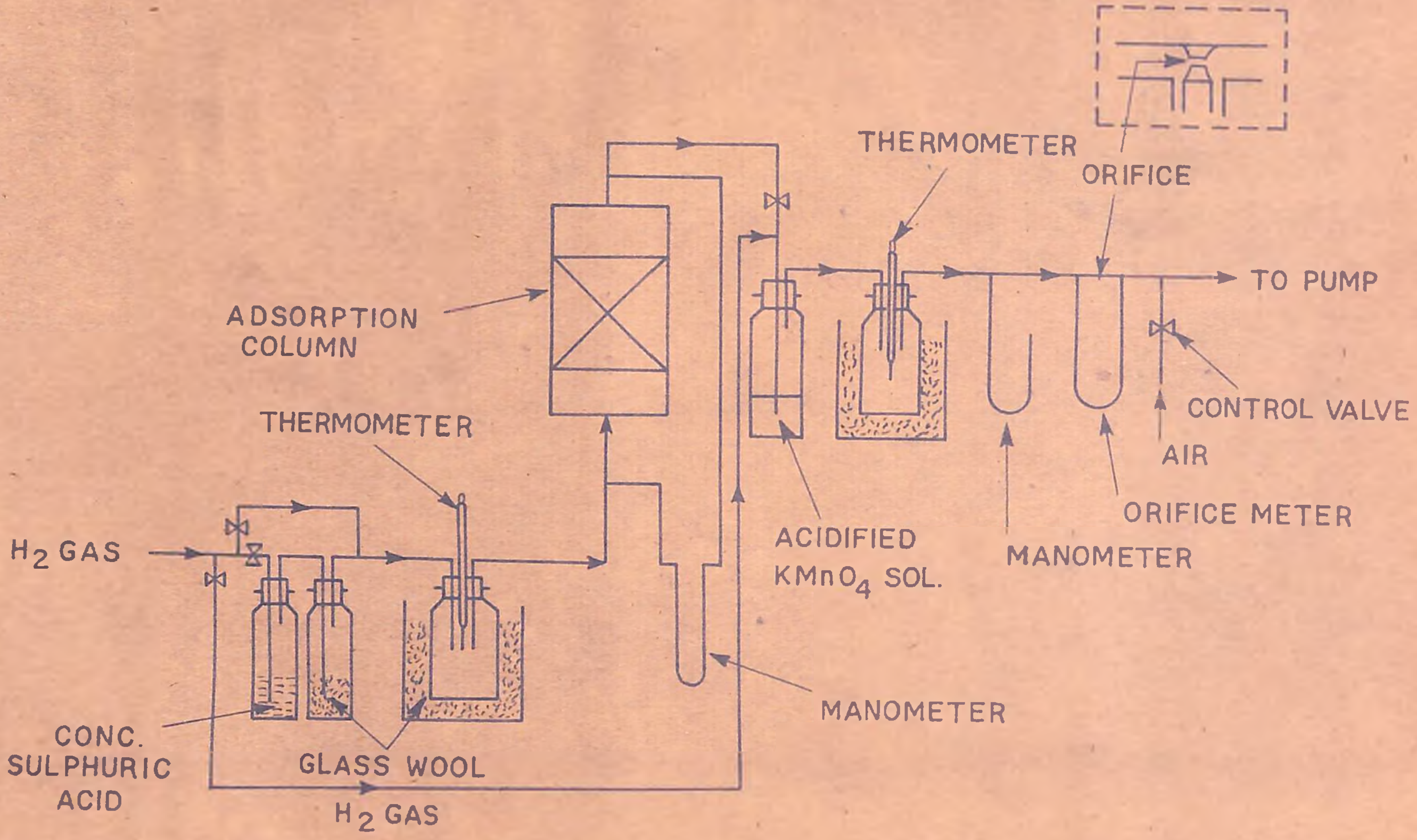


FIG. 8.1 EXPERIMENTAL SET UP : MERCURY REMOVAL FROM H_2 GAS BY ACTIVATED CHARCOAL ADSORPTION TECHNIQUE

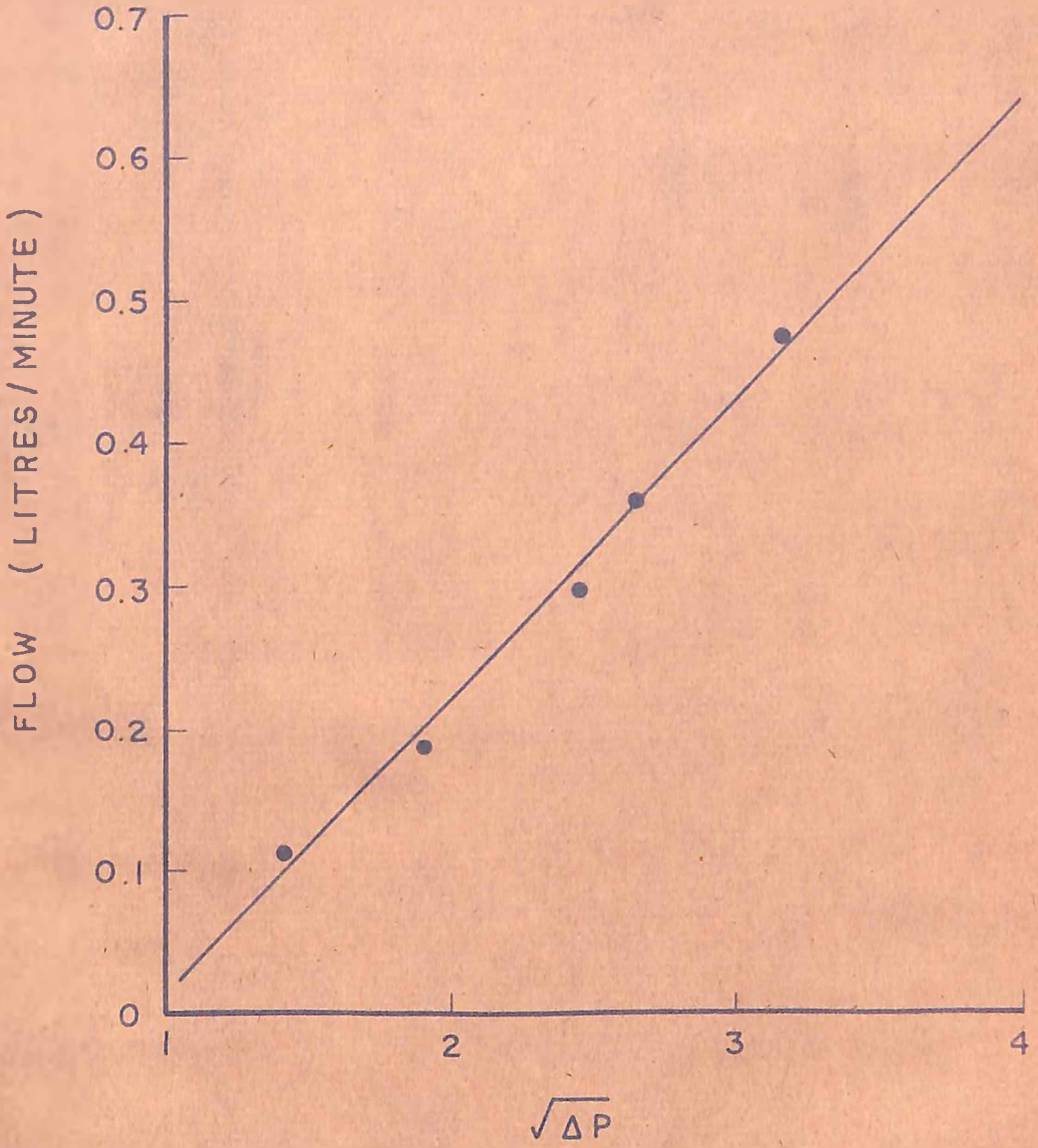


FIG. 8.2 CALIBRATION OF ORIFICE FOR H_2 FLOW.

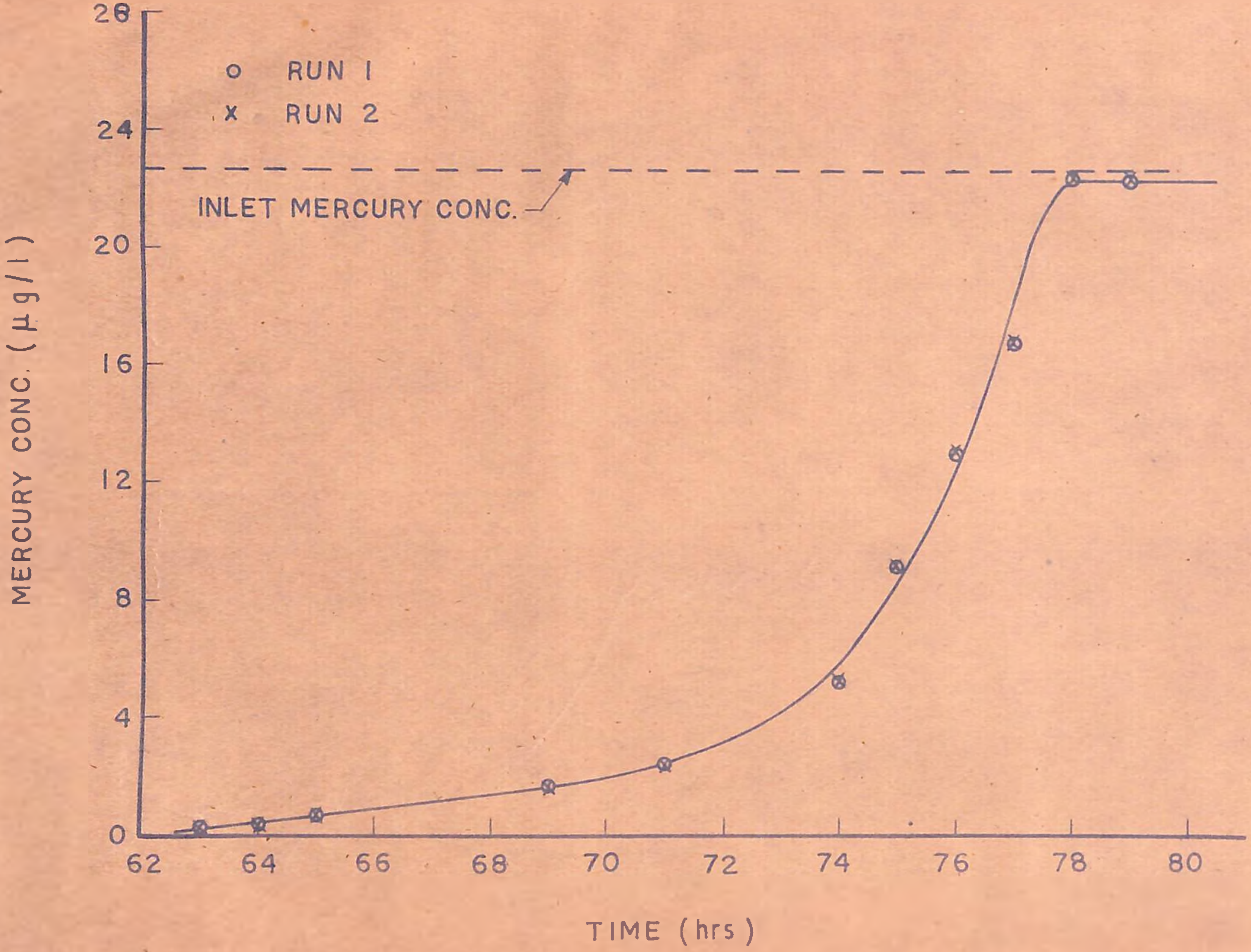


FIG. 8.3 BREAK THROUGH CURVE FOR Hg ADSORPTION ON ACTIVATED CARBON (CARRIER GAS H_2).

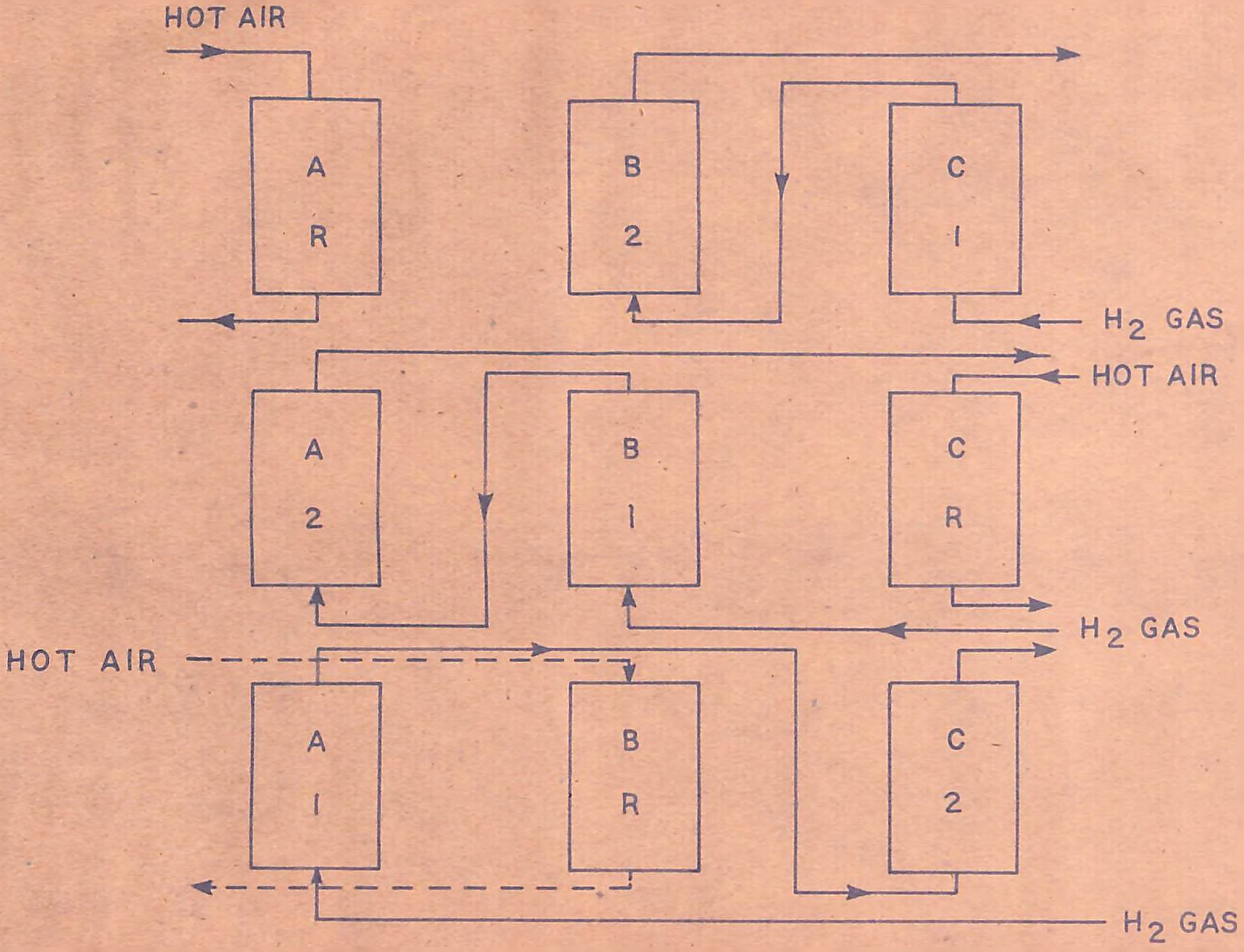


FIG. 8.4 SEQUENCE OF ADSORPTION OPERATION IN A THREE STAGE CASCADE SYSTEM

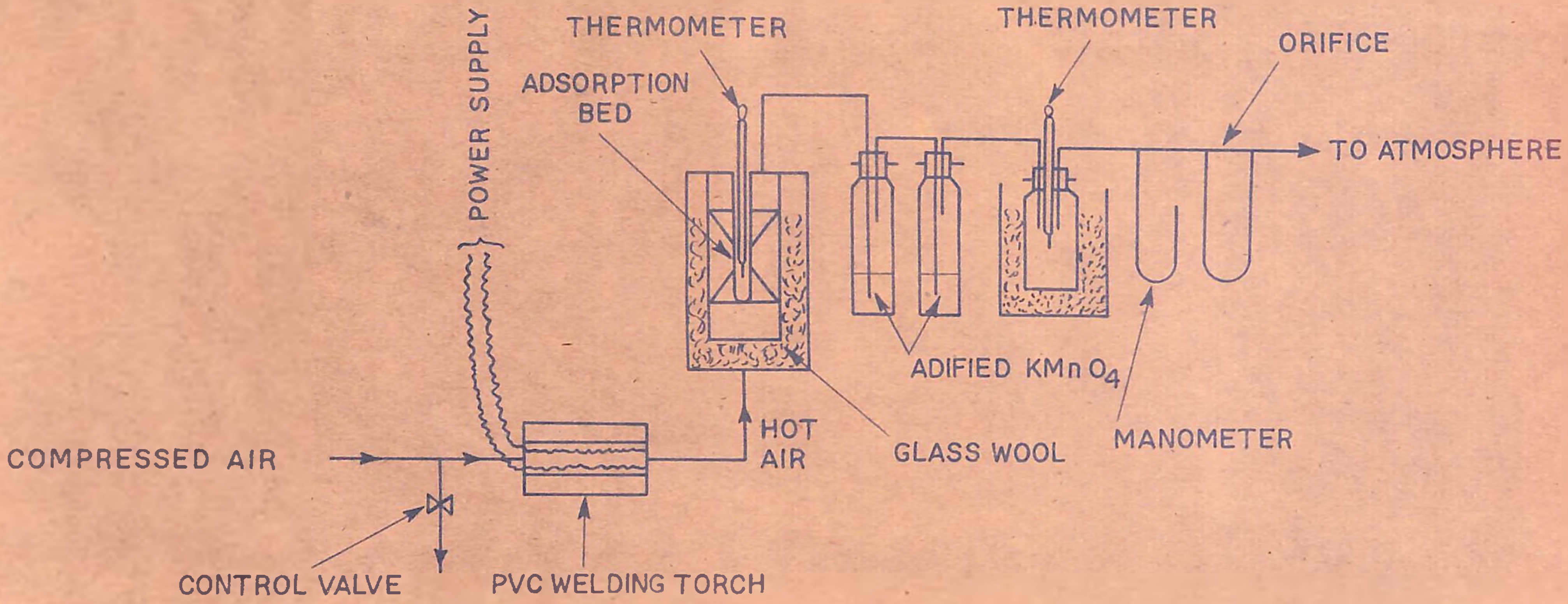


FIG. 8.5 EXPERIMENTAL SET UP : DESORPTION OF SPENT ACTIVAED CARBON BY HOT AIR.

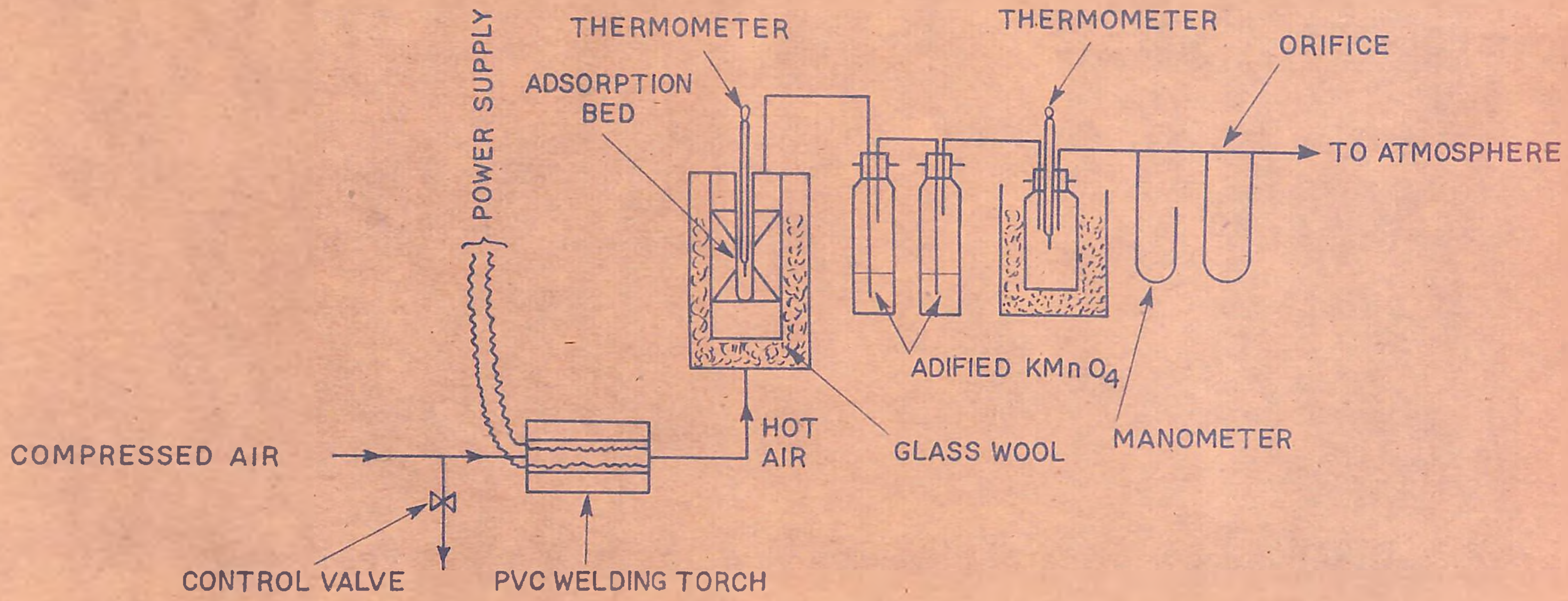


FIG. 8.5 EXPERIMENTAL SET UP : DESORPTION OF SPENT ACTIVAED CARBON BY HOT AIR .

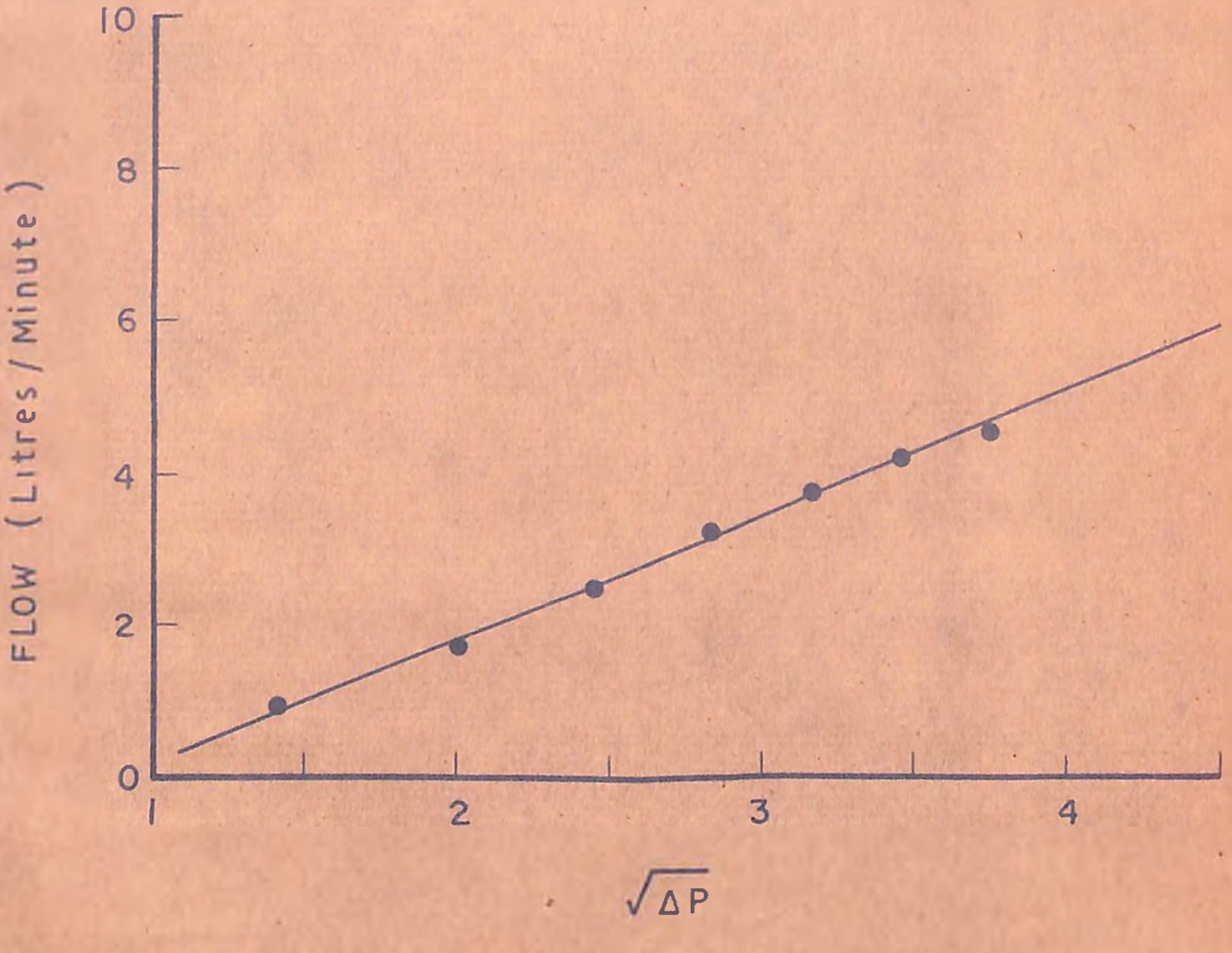


FIG. 8.6 CALIBRATION OF ORIFICE FOR AIR FLOW.

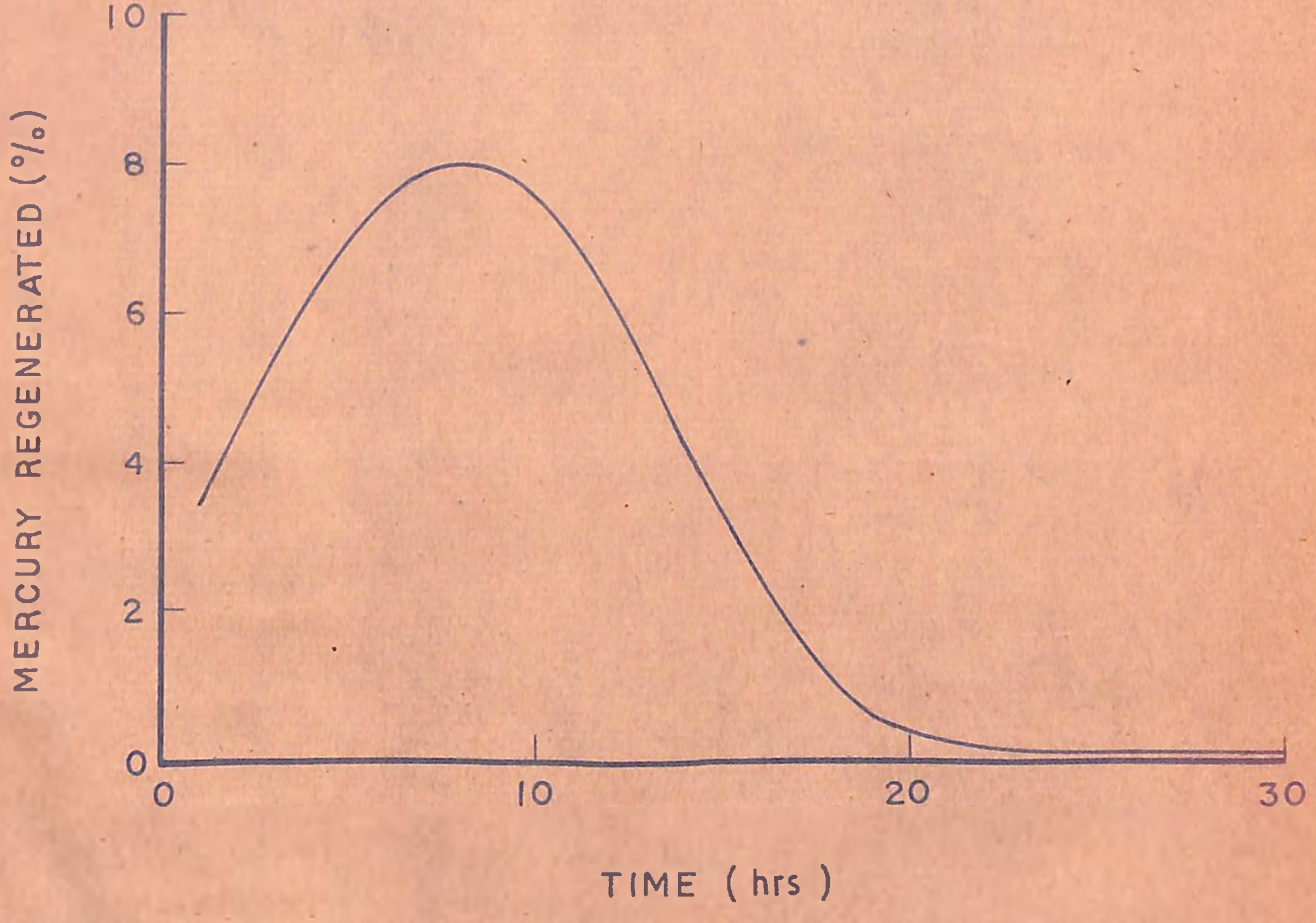


FIG. 8.7 REGENERATION OF SATURATED BED.

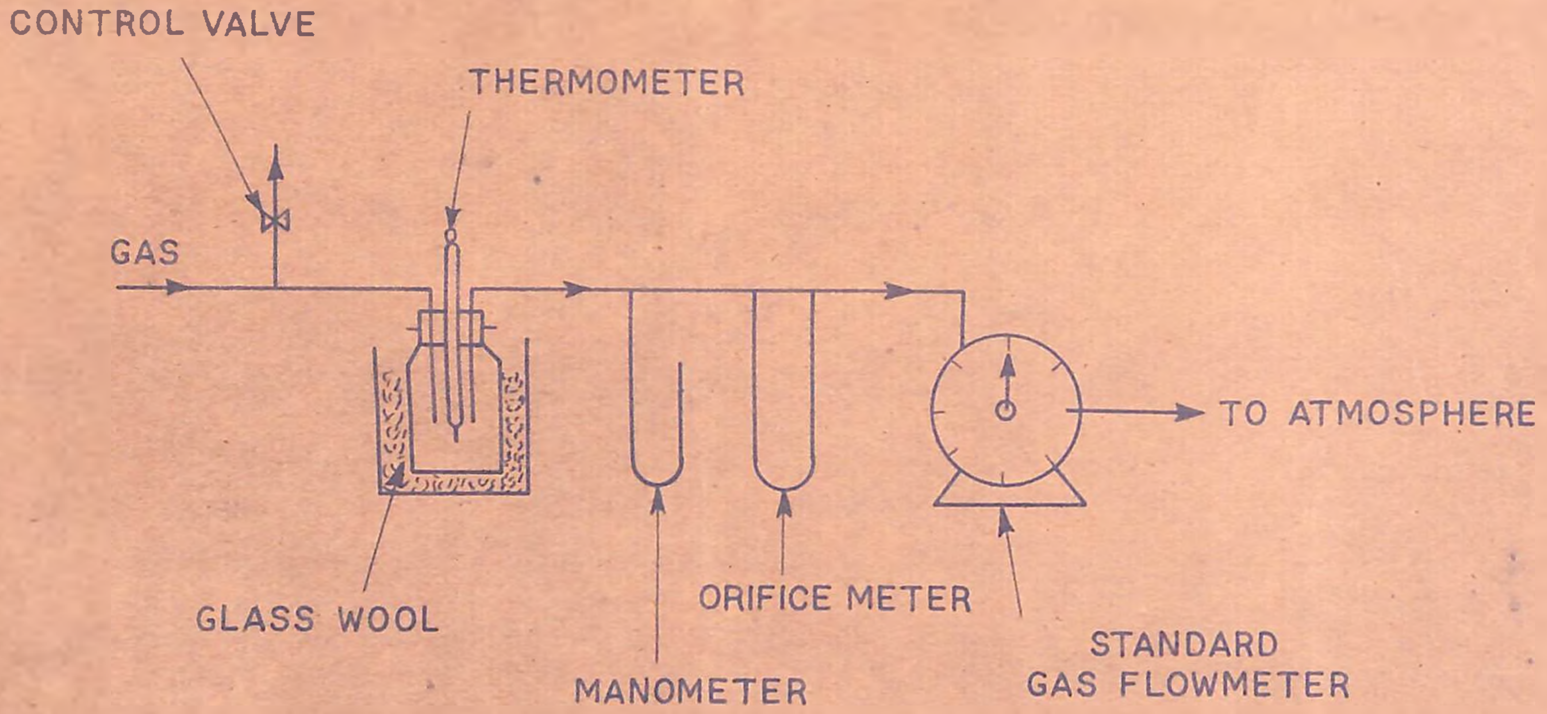


FIG. 8.8 EXPERIMENTAL SET UP: ORIFICE CALIBRATION

CONCLUSIONS

9. CONCLUSIONS

9.1 Mercury Balance:

Brine sludge accounts for 87.9%, hydrogen and hydrochloric Acid Section 5.2%, cell cleaning waste water 3.1% and other miscelleneous sources 3.8%.

9.2 Mercury Recovery from Brine Sludge:

(i) Chlorine treatment technique was found tto be the most pr8mising technique for the plant studied.

(ii) For 1 kg. of sludge a chlorine flow of 0.62 g/mt. for 5 minutes and additional 50 minutes agitation followed by filteration and washing of the treated sludge results 80% mercury recovery. About 239 kg/day of chlorine will be required for treatment of the complete sludge.

(iii) The quality and quantity of the chlorinated sludge filterate was found to be suitable for recycle into feed brine.

9.3 Recycle of the cell cleaning Waste Water:

The quality and quantity of the cell cleaning waste water was found to be suitable for its recycle to the brine system. It was also found that this recycle should be done for first 50 mintues because this time accounts for all Hg lost in waste water resulting during a cell cleaning operation.

9.4 Mercury Recovery from Hydrogen gas:

(i) Mercury in dry hydrogen can be reduced to non-detectable levels by activated carbon adsorption technique.

(ii) Mercury adsorption capacity to break point of the activated carbon used was found to be 0.374 gms of Hg/kg of activated carbon. Activated carbon particle size of 4/16mesh was found suitable for this purpose.

(iii) Break through curve for the Hg adsorption system studied was shallow and use of two activated charcoal beds in series in a three stages cascade system was found to effectively utilize the activated carbon for Hg adsorption.

(iv) Using hot air as eluting agent the spent carbon can be reactivated in 18 hrs only. A bed temperature of 100°C was found to be suitable alongwith hot air flow through the bed equivalent to a flow of 181.7 liters per hr. of air at STP.

(v) There was no detectable decrease in the adsorption capacity of the activated carbon due to repeated use after regeneration with hot air.

9.5 Implimentation of techniques studied in this work will result 88% recovery of the total Hg losses in the plant.

COMPREHENSIVE SCHEME FOR MINIMIZING MERCURY LOSSES IN THE PLANT (RECOMMENDATIONS)

10. COMPREHENSIVE SCHEME FOR MINIMIZING MERCURY LOSSES IN THE PLANT (RECOMMENDATIONS):

Recommendations given in this chapter are not only based on the conclusions made in the preceding chapter but also to some practical experience in the plant.

I. Brine House:

(i) Brine sludge before it is processed for brine recovery by vacuum filter should be chlorinated. Chlorinated sludge should then be filtered using the same drum filter and filterate including adequate washings should be recycled to electrolysis cells. A flow sheet of the suggested scheme has been shown in figure 10.1. Also since Hg loss in this sludge on the days of power failures was found to be as much as 10 times of that lost on normal days, chlorination can be limited to times of power failures.

(ii) Extra care should be taken for proper maintenance of the brine handling equipments to avoid brine leakages, as it contains dissolved Hg.

(iii) Sludge pits should be lined with suitable material to avoid seepage of Hg bearing brine.

II. Cell House:

(i) Cell cleaning waste water obtained for the first 50 minutes (till it becomes visibly clear) should be recycled to sludge pits. It can be mentioned here that this suggestion has already been implemented by the host organisation and is working satisfactorily.

(ii) Garbage etc. removed from the cell house floor should be collected in trays and should be washed with water to recover entrapped metallic mercury.

(iii) Instead of a series of small troughs in the cell house drain system there should be a bigger tank for an efficient sedimentation of any loose metallic mercury.

III. Hydrogen gas:

(i) Mercury contaminated hydrogen gas after drying with conc. sulfuric acid should be processed for Hg removal by using two adsorption beds in series in a three stage cascade system. The size of these beds can be obtained from the adsorption capacity of the charcoal and the time fixed for adsorption cycle. While fixing the adsorption cycle it should be kept in mind that the time taken for regeneration of the bed is 18 hrs.

(ii) The spent carbon bed should be regenerated with hot air and the eluent emerging from the bed should be cooled to condense and recover Mercury. (Scheme shown in Fig.10.2).

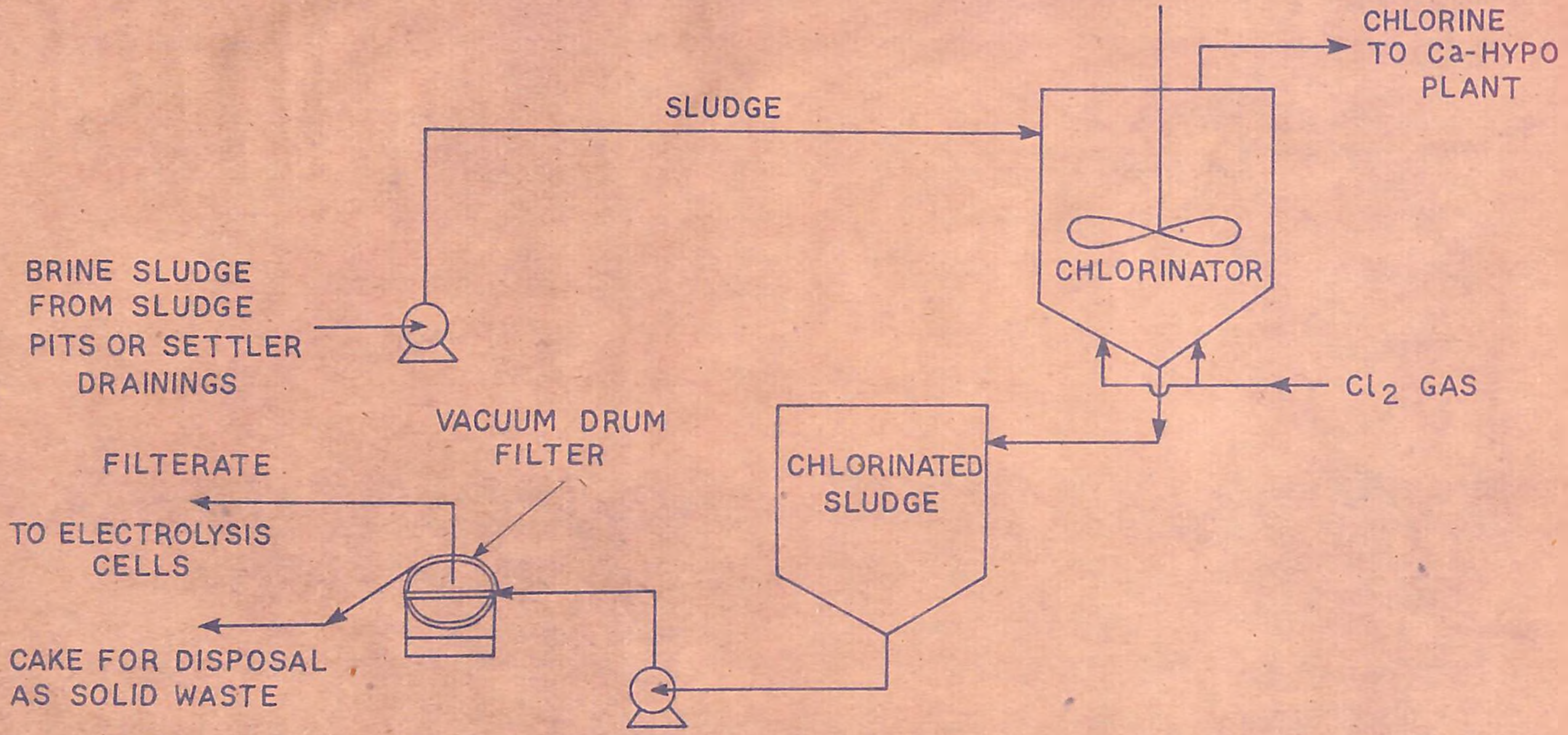


FIG. 10.1 PROPOSED SCHEME FOR MERCURY RECOVERY FROM BRINE SLUDGE

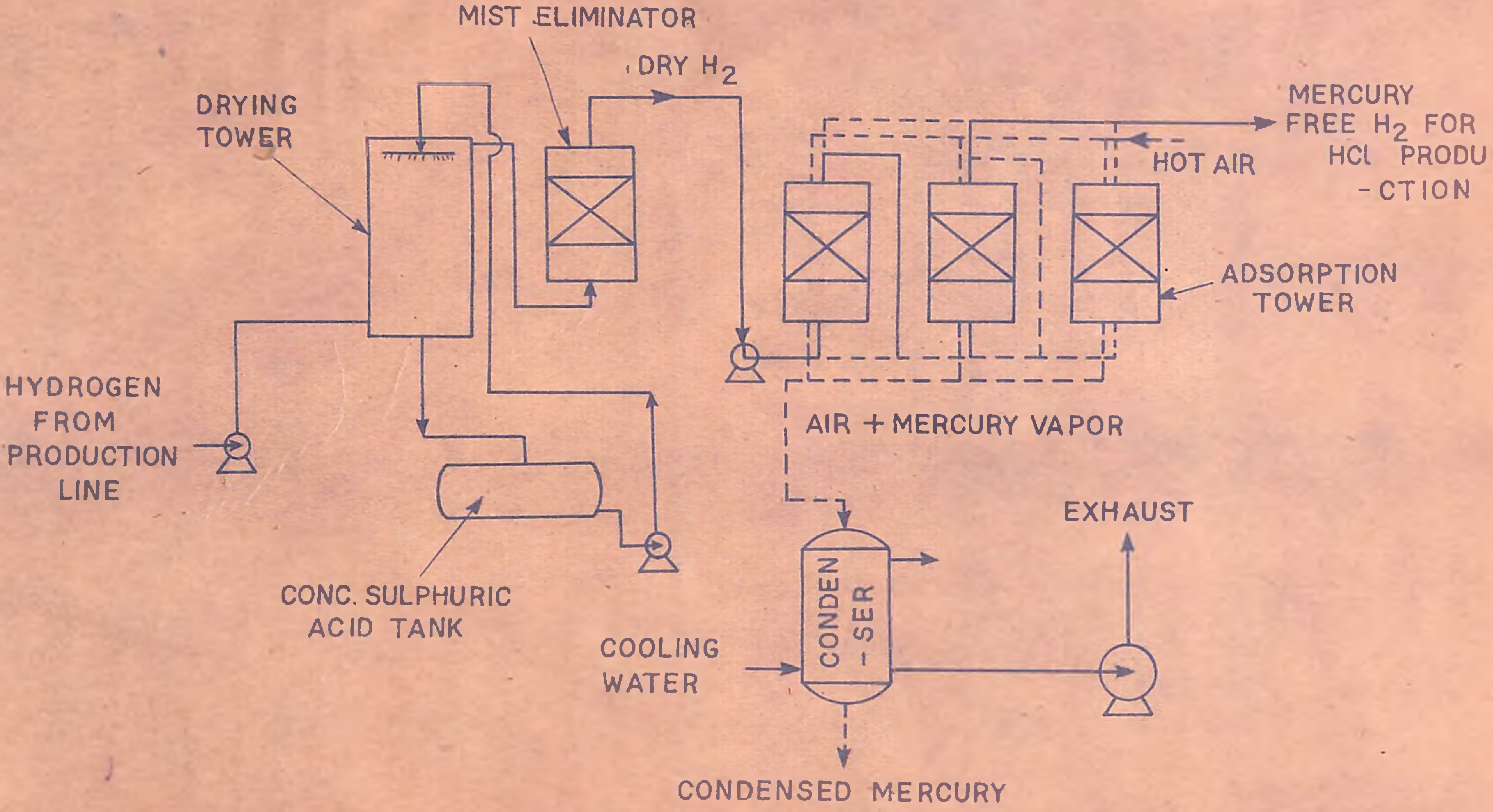


FIG. 10.2 PROPOSED SCHEME FOR MERCURY RECOVERY FROM HYDROGEN GAS

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