

LABORATORY SET-UP FOR ELECTROLYTIC
HYPOCHLORITE GENERATION

(Prepared for International Reference Centre
for Community Water Supply and Sanitation,
Rijswijk Z.H., The Netherlands).

by

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241.3-83LA-19280

PVC spacers
nylon bolts



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Nomor/Ref. : 030/JTA/H/84

Bandung, March 30th, 1984

Lampiran/Appendix : --

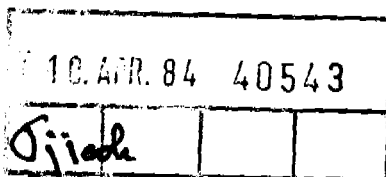
International Reference Centre

Perihal/Subject : --

P.O. Box 5500

2280 HM - RIJSWIJK

The Hague - The Netherlands



Attn. Ir. Tjiok Tiau Kien

Your ref. 32.243 dated Febr.9,1984.

Dear Ir. Tjiok,

The answers of your inquiries about the "Laboratory Set-up for the Electrolytic Hypochlorite Generation" proposed by our group are as follows:

a. Pump rating:

The required pumphead is 1m water at a maximum capacity of 8 litres/min.

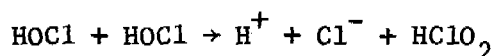
The normal flowrate used in the experiment is 3 litres/min.

b. Fig. 2-4 on p.6-e is a misprint. It should read Fig. 2-3. The solvent used for gluing plexiglass is dichloroethane.

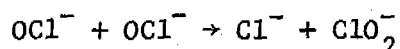
The bolts and nuts and washers are made of Titanium.

c. Small amount of chlorite can indeed be formed in the solution as the result of the disproportioning reactions:

In acid media



In basic media



d. The Orsat analysis is described in Vogel, A.I., "Quantitative Inorganic Analysis, 2nd edn., Longmans, Green & Co., London, 1957.

e. Dimensionally Stable Electrodes commonly used in practice are made of Titanium plate coated with Pt or Titanium plate coated with oxides, such as Ru O₂, In₂ O₃, Ta₂ O₅ etc.

f. Salt quality

Besides solid contaminants kitchen salt contains various metal ions such as Fe, Zn, Cu, Ca, Mg etc. At low concentration ions of Fe, Cu, Ni and Co may catalyze the decomposition reactions of hypochlorite. A concentration of 1 mg/ltr. of Fe respectively 1 mg/ltr of Ni in the solution is enough to effect the acceleration of the decomposition reaction of hypochlorite.

In a dilute salt solution (< 10%) the concentrations of Fe and Ni are usually



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lower than those mentioned above, so that the presence of Fe, Co and Ni ions in the electrolytical process of dilute salt solution can be neglected. The case is different with Ca and Mg ions, in that those ions are present in a rather large amount in the salt. Their concentration varies with the quality of the salt between 0,4% and 1%. The chemical influence of Ca and Mg on the electrolysis of salt solution has not been known yet. Experimental results have shown that the presence of Ca^{2+} and Mg^{2+} in the salt solution may disturb the electrolytical process by forming deposits of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ at the electrodes when the pH in the cell is ca. 11. These deposits would cause clogging of the solution exit of the cell, giving a decrease in the current efficiency as the overall result.

Analysis of a sample of the so called "people salt" (salt prepared from brine by the people by solar evaporation):

Items	Concentration
Mg^{++}	0,6 %
Ca^{++}	0,4 %
Fe^{++}	0,0003 %
Zn^{++}	0
Cu^{++}	0

g. Example of experimental results.

The following results are based on the use of salt of which the analysis is given in f.

g.1. Operating condition.

Distance between the electrodes	, d	: 0,05 dm
Voltage	, v	: 6 volt
Concentration of NaCl in the feed	, Co	: 2,4 %
Volumetric flow rate of the soln	, QL	: 19,5 litres/hour
Temperature of the feed	, T_L in	: 27 °C
Barometric pressure	, p	: 690 mmHg



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g.2. At steady conditions the following results were obtained:

Operation time	,	t	:	2,8 hours
Electric current	,	I_t	:	16,5 Ampere
Energy required during the operation time (2,8 hours)	,	K	:	0,501 kWh
Temperature of the exit liquid	,	T_{L0}	:	29,4 °C
Concentration of NaOCl in the product	,	(NaOCl)	:	682,6 ppm
Concentration of NaOCl ₂ in the product	,	(NaOCl ₂)	:	0 ppm
Concentration of NaOCl ₃ in the product	,	(NaOCl ₃)	:	0 ppm
Volumetric flow rate of the gas	,	Q_G	:	8,9 liters/hours
Concentration of O ₂ in the product gas	,	X_{O_2}	:	0,149
Concentration of H ₂ in the product gas	,	X_{H_2}	:	0,833

g.3. Calculated results:

$$\text{Current efficiency } \eta_{OCl^-} = \left(\frac{(\text{NaOCl})}{1000} \cdot \frac{Q_L \cdot 2(96500)}{74.46} \right) / I_t \cdot 100 \%$$

$$\eta_{OCl^-} = \left(\frac{682,6}{1000} \cdot \frac{19,5}{3600} \cdot \frac{2 \cdot 96500}{74.46} \right) / 16,5 \cdot 100\% = 58,1 \%$$

$$\eta_{O_2} = \left(\frac{X_{O_2} \cdot Q_G \cdot p (273) (4) (96500)}{760 (273 + T_G) 22,4} \right) / I_t \cdot 100\%$$

$$= \left(\frac{14,9}{100} \cdot \frac{8,9}{3600} \cdot \frac{690(273)(4)(96500)}{760(273 + 29,4) \cdot 22,4} \right) / 16,5 \cdot 100\% = 31,5\%$$

$$\eta_{H_2} = \left(\frac{X_{H_2} \cdot Q_G \cdot p (273) (2) (96500)}{760(273 + T_G) (22,4)} \right) / 16,5 \cdot 100\%$$

$$\left(\frac{83,3}{100} \cdot \frac{8,9}{3600} \cdot \frac{(690)(273)(2)(96500)}{760(273 + 29,4)(22,4)} \right) / 16,5 \cdot 100\% = 88,1\%$$

$$E = \frac{K}{(\text{NaOCl}) Q_L t (10^{-6})} \quad \text{kwh/kg NaOCl}$$

$$= \frac{0,501}{692,6 \cdot 19,5 \cdot 2,8 \cdot 10^{-6}} = 13,25 \text{ kwh/kg Na OCl}$$

$$S = \frac{C_o}{(\text{NaOCl}) 10^{-4}} \quad \text{kg NaCl/kg NaOCl}$$

$$= \frac{2,4}{692,6 \cdot 10^{-4}} = 34,65 \text{ kg NaCl/kg NaOCl}$$



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You could insert the above informations in the proposed text of
"Laboratory Set-up for the Electrolytic Hypochlorite Generation"
whenever you wish.

If there is any more question about the set-up, please let us know and we
would be pleased to do our best to answer it.

Lastly but not least we would like to convey our thanks for the literatures
enclosed in your last letter, and for the money that we have just received
recently.

With best regards.

Yours sincerely,

Sudarno

OUTLINE

A description is given regarding a laboratory set-up which is suitable for carrying out experiments to generate sodium hypochlorite by electrolyzing aqueous solution of kitchen salt. A process flow diagram, equipments specifications and sketches are given.

Processes taking place at the surface of the electrodes as well as those occurring in the solution are described. Parameters affecting the performance (current efficiency) of the electrolytic cell are stipulated. Since many of the parameters have contradictory effects with regard to the processes taking place in the cell, it is essential that the optimum value of the parameters be determined experimentally. Analytical procedures are given, they are eventually referred to some publications.

Methods of calculation and some exercises are also included.

I. INTRODUCTION

The use of "On Site Hypochlorite Generators" to produce disinfectant has become more and more attractive, especially in the developing countries, relative to the use of conventional disinfectants, such as chlorine gas and caporit, because of several reasons. Chlorine gas is a good disinfectant and needs relatively little operation cost to use it as a disinfectant. Nevertheless because of its high toxicity and corrosive nature when used in wet condition, it needs a skilled labor to handle. Whereas calcium hypochlorite for most developing countries is still an import commodity, which is available only in some big cities.

A solution of sodium hypochlorite has a high oxidation power similar to chlorine gas and other hypochlorite salts. This property has been utilized in various applications, such as bleaching and disinfection. Usually sodium hypochlorite is obtained as a dilute aqueous solution, and is unstable in the sense that it dissociate easily, making it unsuitable for production in large quantities and for long period storage. These drawbacks can be overcome by producing NaOCl solution at the place where it is being used. In this way the use of sodium hypochlorite as a disinfectant can be more advantageous than caporit and chlorine gas.

II. ON-SITE HYPOCHLORITE GENERATION

One way of producing sodium hypochlorite is to electrolyze aqueous solution of kitchen salt in an electrochemical cell using inert electrodes and no diaphragm. The solution obtained in this way does not have a concentration of sodium hypochlorite as high as that produced chemically, nevertheless it is sufficient to meet various needs.

To operate such a cell one must try to accomplish the following aims:

- a. to obtain a high electric current efficiency,
- b. to obtain a high conversion of NaCl into NaOCl.

Parameters affecting the current efficiency and the conversion comprise the followings:

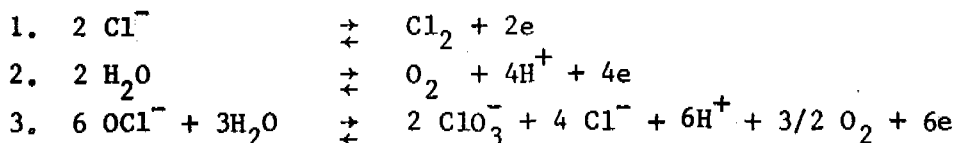
- a. Operating conditions
- b. Electrode materials
- c. Cell geometry

II.1. Electrode Processes

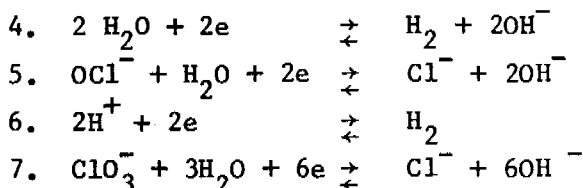
The principal electrode processes which take place during the electrolysis under the conditions which are favorable for the pro-

duction of hypochlorite are as follows:

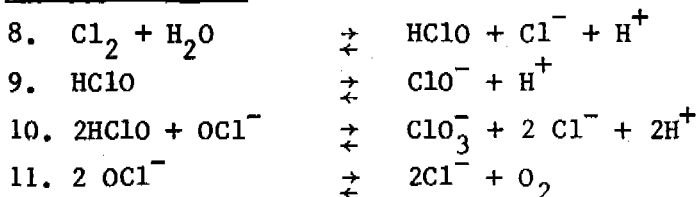
At the anode



At the cathode



In the Solution



Equations 2, 3, 5, 7, 10 and 11 form the unwanted side reactions causing a decrease of the current efficiency.

Reaction 11 is catalyzed by heavy metal ions, such as Fe and Cu ions, and is the principal reaction causing the dissociation of hypochlorite during storage.

The formation of chlorate in the solution through reaction 10 is favored by high temperature (> 40°C) and low pH, because at low pH both HOCl and OCl⁻ are available in the solution. Reaction 2, 3, 5 and 7 taking place at the electrode's surface are influenced by the operating conditions (concentration of NaCl, Voltage, solution flow rate) as well as by the electrodes material. Other side reactions causing a decrease of the current efficiency are those forming hydroxides from Mg²⁺ and Ca²⁺ ions which take place in the surrounding of the cathode. The hydroxides will form a deposit on the surface of the cathode causing an increase of the over voltage and a decrease of the current efficiency.

II.2. Operating Conditions

The operating conditions play an important role in increasing the current efficiency and thus decreasing the required kWh, as well as in decreasing the salt requirement. Parameters which have strong influences on the current and the salt efficiencies are:

- a. Concentration of NaCl in the feed solution
- b. Voltage between the electrodes
- c. Current density
- d. Flow rate of the feed solution
- e. Distance between the electrodes
- f. PH of the solution
- g. Temperature of the solution

The rate of formation of hypochlorite is linearly proportional to the electric current flowing through the solution in the cell. While keeping the other variables constant, the electric current can be increased by increasing the salt concentration in the feed or the voltage between the electrodes, as well as by decreasing the distance between the electrodes. An increase of the solution temperature may result in an increase of the electric current as well. Furthermore reactions 2, 3 and 5 are retarded by using high concentrations of salt.

Operating the cell at high voltage enhances the unwanted side reactions, whereas operating at high temperature increases the formation of chlorate and the consumption of the electrodes resulting in the accelerated deterioration of electrodes.

By decreasing the distance between the electrodes the current efficiency is increased, and the time for the OCl^- ion to travel to the electrode's surface is shortened as well resulting in the acceleration of reaction 3 at the anode and reaction 5 at the cathode.

For a given hypochlorite cell there exists an optimum electrolyte flow rate giving the highest current efficiency. At low flow rate the diffusion of Cl^- ion to the anode is slow and thus the rate of the hypochlorite formation is also slow. Conversely at very high flow rate the possibility for Cl_2 to reach the surface of the cathode and for OCl^- to reach the surfaces of the anode and the cathode is increased. In such a case the reversed reaction of Cl_2 producing Cl^- ion at the cathode and reaction 3 at the anode as well as reaction 5 at the cathode cannot be avoided. However at high solution flow rate the deposition of $Ca(OH)_2$ and $Mg(OH)_2$ at the cathode surface is reduced, and this induces some advantages. First the current efficiency can be increased and second the frequency for washing the cell with acid is reduced resulting in a longer life of the electrodes.

Likewise the pH of the solution has negative as well as positive influences on the process as well. At low pH most of the hypochlorite exists in its acid form, so that the possibility of the occurrence of the reaction consuming OCl^- at that pH is diminished, conversely the reaction for the formation of chlo-

rate (reaction 10) is accelerated. Each variable, whatever value it has seems to exert some influences which have contradictory effects. It is therefore highly recommendable that for any hypochlorite cell the optimum operation variables be determined experimentally.

II.3. Material for the electrodes

The choice of the construction material for the electrodes determines the current efficiency as well as the lifetime of the electrodes.

The current efficiency is determined for each electrode material primarily by the values of the overpotential of the various compounds involved in the reactions. The overpotential of a reaction is the potential in excess of the equilibrium potential (E^0) of that reaction which has to be provided in order that the electrochemical reaction takes place. In electrode processes overpotential means energy required to transfer ions from the bulk of the solution to the surface of the electrodes whereby electron transfers and chemical reactions form a stable products. The magnitude of the overpotential depends on the type of the ions involved in the reaction and the material of which the electrodes are made.

The electrodes must be prepared in such a way that the overpotentials of the side reactions which are in competition with the desired reactions, are as high as possible. In such a case the cell is expected to run with a high current efficiency. One reason why Platinum is oftenly chosen as the material for the electrodes of hypochlorite cells is the relatively high value given by Pt for the difference between the overpotentials of the O_2 formation and the Cl_2 formation. Hence the current loss due to the formation of O_2 (reaction 2) can be suppressed.

II.4. Cell Geometry

The form of the cell as well as the form and the geometrical arrangement of the electrodes are factors which can influence the process variables such as the flow rate and the hydrodynamics, the distance between the electrodes, the current density etc. Another consideration for choosing the form of the cell is the possibility for avoiding the occurrence of stagnant pockets of liquid in the cell which will enhance deposition of $Mg(OH)_2$ and $Ca(OH)_2$ on the surface of the cathode.

III. EXPERIMENTAL

The experiment is designed primarily for studying the influences of some process variables on the performance of a cell, in which performance is expressed as the current efficiency, the energy consumption and the salt consumption of the cell.

The followings are the process parameters which can be varied during the experiments:

- a. Salt concentration of the feed
- b. Voltage between the electrodes
- c. Flowrate of the electrolyte solution
- d. Distance between the electrodes
- e. PH of the solution
- f. Hypochlorite concentration in the feed
- g. Temperature of the solution.

III.1. Equipments

The equipment set-up is given in figure 1. The followings are the description of the equipments.

a. Feed Tank (T_1) and Product Tank (T_2)

Function : the feed tank (T_1) is used for the storage of the feed solution;
the product tank (T_2) is for storing the product solution.

Type : cylindrical vessel provided with cover

Quantity : T_1 - one
 T_2 - one

Capacity : 100 litres to 200 litres for each tank

Dimension : unspecified

Material : fibre glass, PVC or HDPE

b. Pump (P)

Function : to transfer the feed solution

Quantity : one

Type : centrifugal

Capacity : 8 litres/min.

Material : material which resists corrosion by brine solution.

Catalog : TAMSON 1145B 1, Circulatie pomp nr. 480.

c. Valve (V_1)

Function : to regulate the flowrate of the feed solution
Quantity : one
Type : needle valve
Capacity : maximum opening 6 mm
Material : glass with Teflon inserts
Catalog : Karl-Kolb 660-423

d. Liquid Flowmeter (F_1)

Function : to indicate the solution flowrate
Quantity : one
Type : rotameter
Capacity : maximum 8 litres/min.
Material : glass
Catalog : Fisher & Porter FP -1/4 - 20G - 5/-CD 14

NOTE: To measure the flowrate of the solution use a measuring cylinder and a stopwatch.

e. Electrochemical Cell (HC)

Function : as an electrochemical reactor
Quantity : one
Type : Morton Biocidal
Material : plexiglass

NOTE: see figures no. 2-1, 2-2 and 2-4 for the details.

Electrodes

Quantity : one pair
Type : Dimensionally Stable Electrodes, flat-type.
Size : 152 mm x 57 mm x 2 mm
Material : for the anode : Ti coated with Pt

for the cathode: Ti

Catalog : Magneto-Chemie
P.O. Box 217-3100 Ae, Schiedam, Holland

NOTE: see figure no. 2-3 for the details.

f. Gas Separator (S)

Function : to separate gas from liquid solution
Quantity : one
Type : spray column with vigreux packing
Size : outside dia. = 6 cm, length = 45 cm
Material : glass

NOTE: see figure 3 for the details.

g. Chlorine Absorber (AC)

Function : to absorb Cl_2 gas which might escape with the gas from the gas separator (S).
Quantity : two
Type : bubble column
Size : outside dia. = 3 cm, length = 12 cm.
Material : glass
Absorbent : NaOH solution, 4 N, 30 cc

NOTE: see figure 4 for the details.

h. Cooler (C)

Function : to cool down the solution leaving the gas separator (S)
Quantity : one
Type : coil type cooler
Size : length = 40 cm
Material : glass
Cooling medium : tap water

i. Water Absorber (AW)

Function : to absorb water vapor from the product gas
Quantity : one
Type : cylindrical column filled with silica gel
Size : length = 20 cm
Material : glass

j. Gas Flow meter (F_2)

Function : to measure the flow rate of the product gas
Quantity : one
Type : bubble column
Size : inside diameter ca. 1 cm;
the column is provided with a mark on each ends,
the volume between the marks is 50 cc.
Material : glass

k. Direct Current Power Supply Unit (R)

Function : to produce low voltage, high amperage direct current
by converting electricity from the main.
Quantity : one
Type : silicon type rectifier
Capacity : 40 A, 14 DCV
NOTE: see figure 5 for the details. (page 25)

III.2. Experimental Procedure

Some preliminary steps must be done before the actual experiment is started. First the rotameter F_1 must be calibrated and second leakages on all of the line and joints must be checked and repaired.

The experiment is started up by switching the pump on allowing the feed solution to flow from the feed tank through the whole set-up. The feed flow rate is regulated using valve V_1 and rotameter F_1 , the latter functions as the flow indicator.

Whenever the flow has become stable, the electric current is switched on allowing the desired voltage drop across the electrodes by manipulating the variac supplied with the rectifier unit R. The amperes and the voltage drop are read from the ammeter respectively the voltmeter. The formation of gas bubbles at the electrodes surface indicates that electrochemical reaction is taking place. Chlorine gas is hydrolyzed fastly in accordance with reaction 8 and 9, whereas hydrogen gas contained in the solution is separated from the liquid in the separator S. The gas free solution flows from the separator S to the cooler C to cool the solution whenever necessary. This cooling is only needed if the product solution is recycled and reused as the feedstock. In this way the influence of the OCl^- content in the feed can be studied. If cooling is not needed, the by-pass line may be used allowing the solution to flow to

product tank T₂ without passing the cooler C. Sampling of the product liquid solution can be done using valve V₆.

The gas coming out of the separator S consists mostly of H₂ and a minor quantity of O₂. However if the contact time between the gas and the liquid, i.e. the time for the mixture to travel from the cell to the separator, is not sufficient, the hydrolyzation of chlorine is not complete and some of the chlorine escapes with the gas leaving the separator S. In that case the escaping chlorine will be caught by the absorbent in the absorber AC where chlorine react with NaOH 4N solution to form NaOCl.

The absent of Cl₂ in the gas leaving the absorbers AC is assumed if no NaOCl is formed in the absorbent of the downstream absorber AC.

In most cases all of the chlorine produced in the cell is completely hydrolyzed and remains in the brine solution. In such a case it is advisable to by-pass the absorbers in order to avoid fluctuation of the gas flow passing through the bubble column gas meter F₂ which makes the gas flow measurement somewhat troublesome.

The gas leaving the absorbers AC enters the water absorber (AW) in which the water vapor is absorbed by silica gel. The dry gas flows then through the gas meter F₂ where the flowrate is measured by observing the time for a gas bubble to pass through the space between the marks put on both ends of the bubble column. The composition of the dry gas can then be analyzed (see par. III.4 for the analytical procedures).

Other variables which are to be observed consist of:

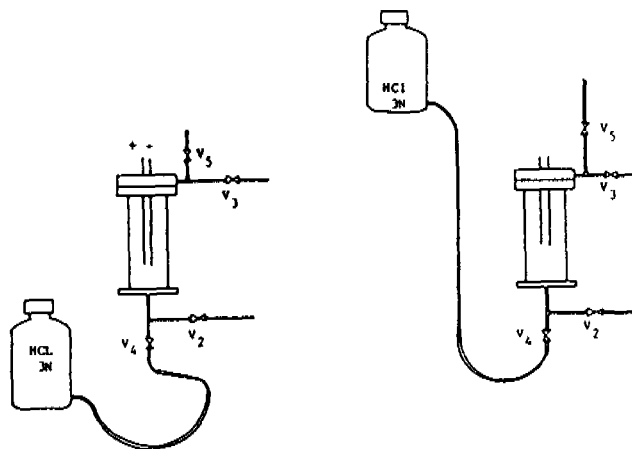
- a. Electric current flowing through the brine solution,
- b. Energy consumed during a given period,
- c. PH of the brine solution.

III.3. Cell cleaning

Due to the evolution of hydrogen gas formed by the combination of electrons and H-ions at the cathode, the solution surrounding this electrode becomes somewhat basic. This increase in pH enhances the deposition of Mg²⁺ and Ca²⁺ in the form of their hydroxides, most of which adheres at the surface of the cathode and some clogs the cell exit. These phenomena result in the decrease of the current efficiency of the cell. It is therefore advisable to clean the cell prior to each experimental run.

Cleaning the cell is done by dissolving the hydroxide deposits in HCl-3N, as described in the following steps.

First the hypochlorite cell must be emptied of the rest of the brine solution by opening valves V_4 and V_5 and closing valves V_2 and V_3 . Next a wash bottle containing the acid is connected with a flexible tubing to valve V_4 . The wash bottle is then raised slowly to such a level that the cell is fully filled with the acid. The acid is kept in the cell until the deposit is completely dissolved. Having done this the cell must then be emptied of the acid and subsequently be washed with water until the acid rest has completely disappeared from the cell. Before starting the next experiment do not forget to close valves V_4 and V_5 and to open valves V_2 and V_3 .



III.4. Analysis

In each experiment the concentration of chlorides in the feed and the concentration of hypochlorites, chlorites and chlorates in the product solution are analyzed. The chloride is determined by the method of argentometry, whereas for the hypochlorite, chlorite and chlorate the biamperometric titration is employed (see appendix for the analytical procedures).

Chlorine which is absorbed in the chlorine absorber (AC) is analyzed by the same biamperometric method after the absorbent solution has been neutralized with H_2SO_4 4N.

The gas product which should contain only H_2 and O_2 is analyzed using an Orsat Apparatus or a gas liquid chromatograph provided with a thermal conductivity detector and a column containing molecular sieve 5A.

The pH of the solution is determined using a pH-meter.

IV. CALCULATION

IV.1. Data

The following data are required for the calculation of the results and hence they should be observed during the experiments.

Variable	Symbol	Unit
Voltage	V	Volt
Electric current	I_t	Ampere
Concentration of NaCl in the feed	Co	Weight %
Volumetric flow rate of the solution	Q_L	litre/second
Volumetric flow rate of the gas	Q_G	litre/second
Concentration of NaOCl in the product	(NaOCl)	ppm
Concentration of NaClO ₃ in the product	(NaOCl ₃)	ppm
Concentration of O ₂ in the product gas	X_{O_2}	mol %
Concentration of H ₂ in the product gas	X_{H_2}	mol %
Length of the electrode	L	dm
Width of the electrode	W	dm
Distance between the electrodes	d	dm
Energy required for a given time	K	kWh
Pressure	p	mm Hg
Temperature of the gas	T_G	°C
Temperature of the feed	$T_{L\text{ in}}$	°C
Temperature of the exit liquid	T_{LO}	°C

IV.2. Calculation of the Current efficiency

The efficiency of the electric current for the formation of molecule i is defined as the ratio between the current required for the formation of molecule i and the total current applied between the electrodes.

The current required for the formation of molecule i is determined by the Faraday law

$$G_i = \frac{a_i I_i t}{zF} \quad \text{or}$$

$$I_i = \frac{G_i zF}{t a_i}$$

in which:

I_i = current required for the formation of molecule i, Amperes

G_i = weight of molecule i produced during time t , gram
 t = time required for the formation of G_i gram molecule i , seconds
 G_i/t = rate of formation of molecule i , gram/second
 z = number of the electrons involved in the formation of molecule i
 a_i = molecular weight of molecule i , gram/mol
 F = Faraday number = 96500 coulombs/gram equivalent

The current efficiency (η_i) can be calculated from the following equation:

$$\eta_i = \frac{I_i}{I_t} \times 100 \%$$

EXERCISE 1: Calculation of the current efficiency of the formation of hypochlorite (η_{OCl^-}).

The current required for the formation of hypochlorite is the same as the current required for the formation of that part of chlorine which is converted to NaOCl.

$$I_{\text{OCl}^-} = I_{(\text{Cl}_2 \rightarrow \text{OCl}^-)} = \frac{G_{(\text{Cl}_2 \rightarrow \text{OCl}^-)}}{t} \cdot \frac{zF}{a}$$

$$\frac{G_{(\text{Cl}_2 \rightarrow \text{OCl}^-)}}{t} = \frac{(\text{NaOCl})}{1000} \cdot \frac{a_{\text{Cl}_2}}{a_{\text{NaOCl}}} \cdot Q_L$$

in which:

$G_{(\text{Cl}_2 \rightarrow \text{OCl}^-)}$ = weight of that part of chlorine which is converted to OCl^- , gram

$I_{(\text{Cl}_2 \rightarrow \text{OCl}^-)}$ = current required for the formation of that part of chlorine which is converted to OCl^- , Amperes.

The number of electrons involved in the formation of chlorine according to reaction 1 is 2 so that:

$$I_{\text{OCl}^-} = \frac{(\text{NaOCl})}{1000} \cdot \frac{a_{\text{Cl}_2}}{a_{\text{NaOCl}}} \cdot \frac{Q_L \cdot 2F}{a_{\text{Cl}_2}} = \frac{(\text{NaClO})}{1000} \cdot \frac{Q_L \cdot 2 \cdot (96500)}{74.46} \text{ A}$$

$$\eta_{\text{OCl}^-} = \frac{I_{\text{OCl}^-}}{I_t} \cdot 100 \%$$

EXERCISE 2: Calculation of the current efficiency of the formation of O_2

$$I_{O_2} = \frac{G_{O_2}}{a_{O_2} t} \cdot zF$$

$$\frac{G_{O_2}}{a_{O_2} t} = X_{O_2} \cdot Q_G \cdot \frac{p \cdot 273}{760(273 + T_G)} \cdot 22.4 \quad \text{moles/second}$$

$$z = 4 \quad (\text{ef. reaction 2})$$

$$\text{So that } \eta_{O_2} = \left[\left(\frac{X_{O_2} \cdot Q_G \cdot p(273)(4)(96500)}{760(273 + T_G) 22.4} \right) / I_t \right] 100 \%$$

IV.3. Calculation of the energy

The energy required for the formation of 1 kg NaOCl is given the symbol E.

During t seconds operation the energy required is K kWh.

The relation between E and K is as follows:

$$E = \frac{K}{(\text{NaOCl}) Q_L t (10^{-6})} \quad \text{kWh/kg NaOCl}$$

IV.4. Calculation of the salt consumption

The salt consumption for the formation of 1 kg NaOCl (symbol S) can be calculated as follows:

$$S = \frac{C_o}{(\text{NaOCl}) 10^{-3}} \quad \text{kg NaCl/kg NaOCl.}$$

V. REFERENCES

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APPENDIX

A. SET OF DRAWINGS

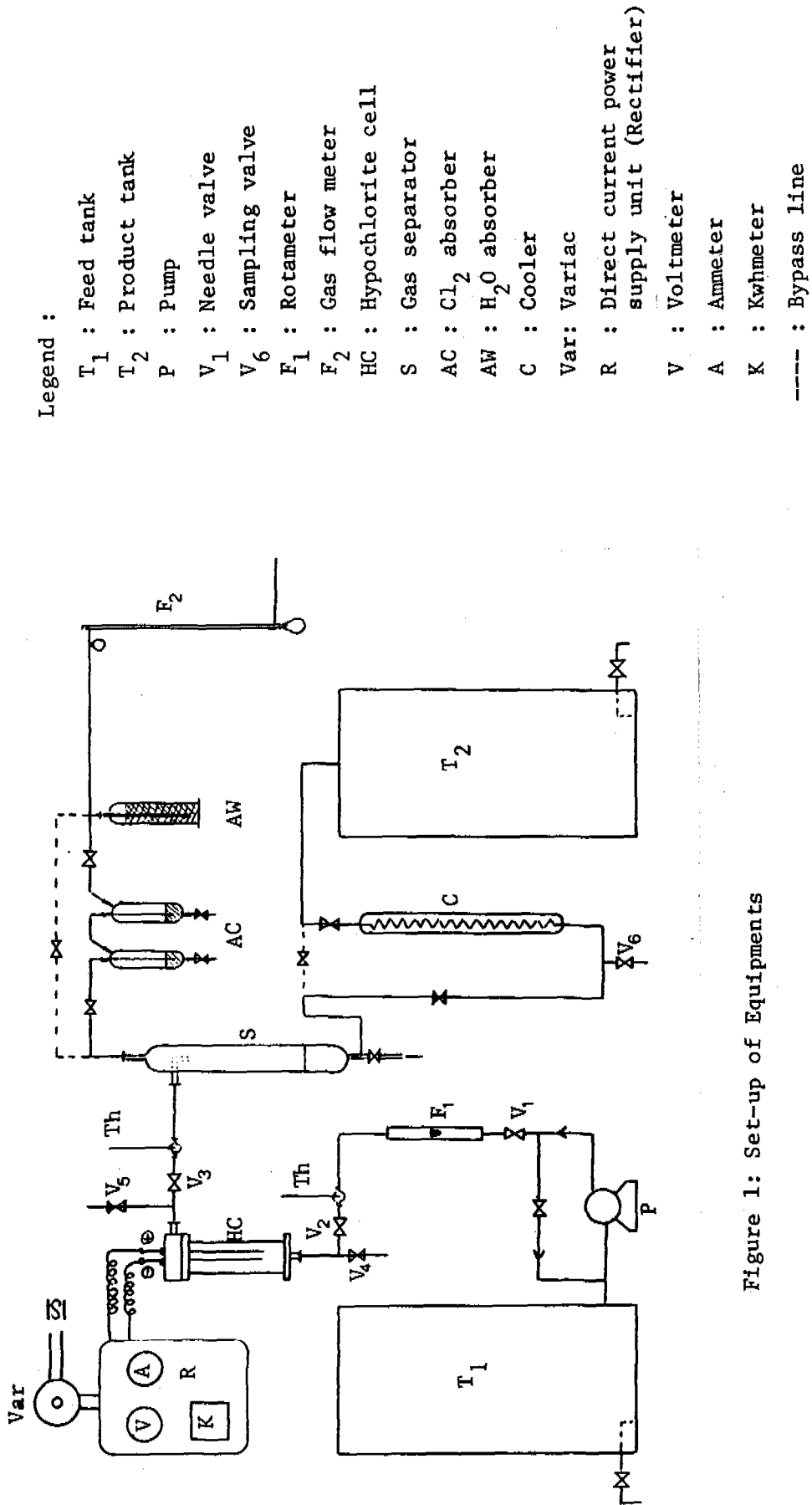


Figure 1: Set-up of Equipments

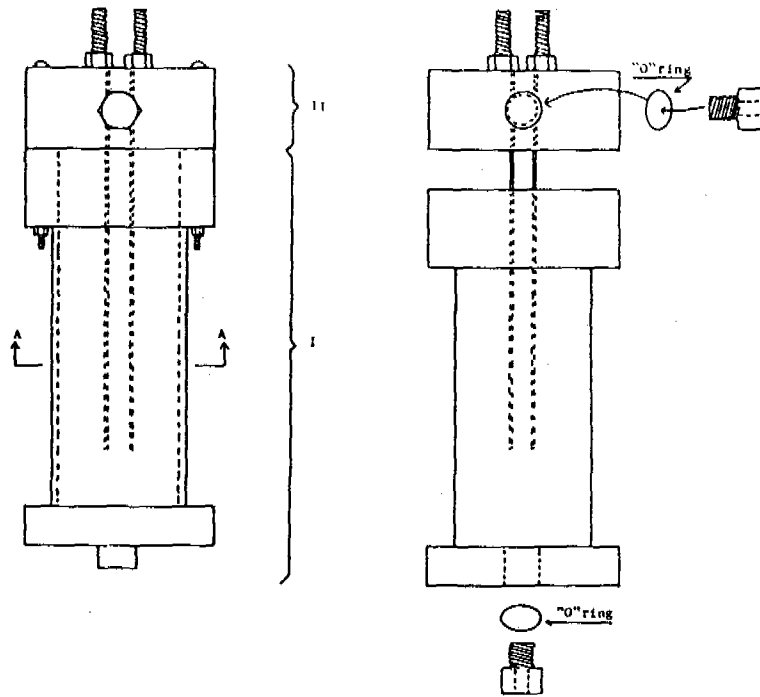
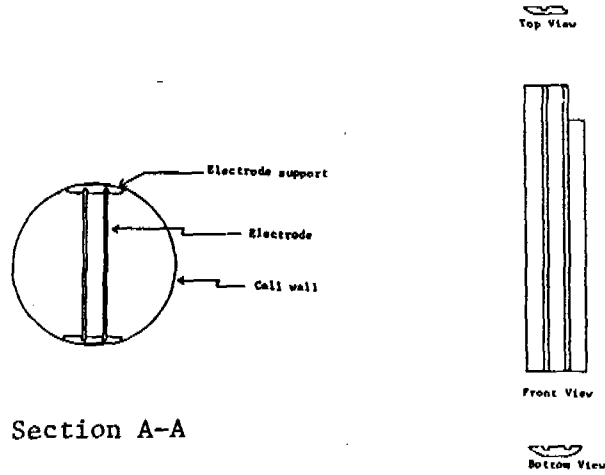


Figure 2-1: Hypochlorite Cell - Overall View
Scale: 1:4



Detail of Electrode Support

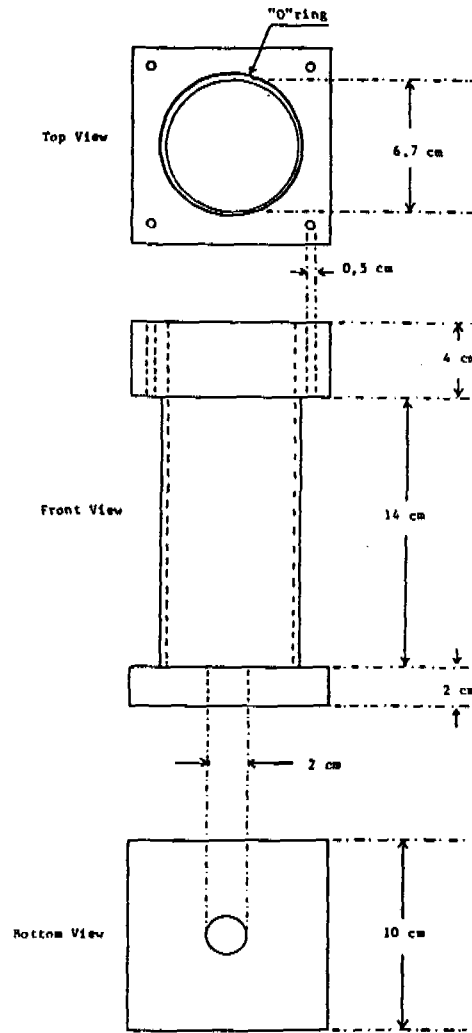
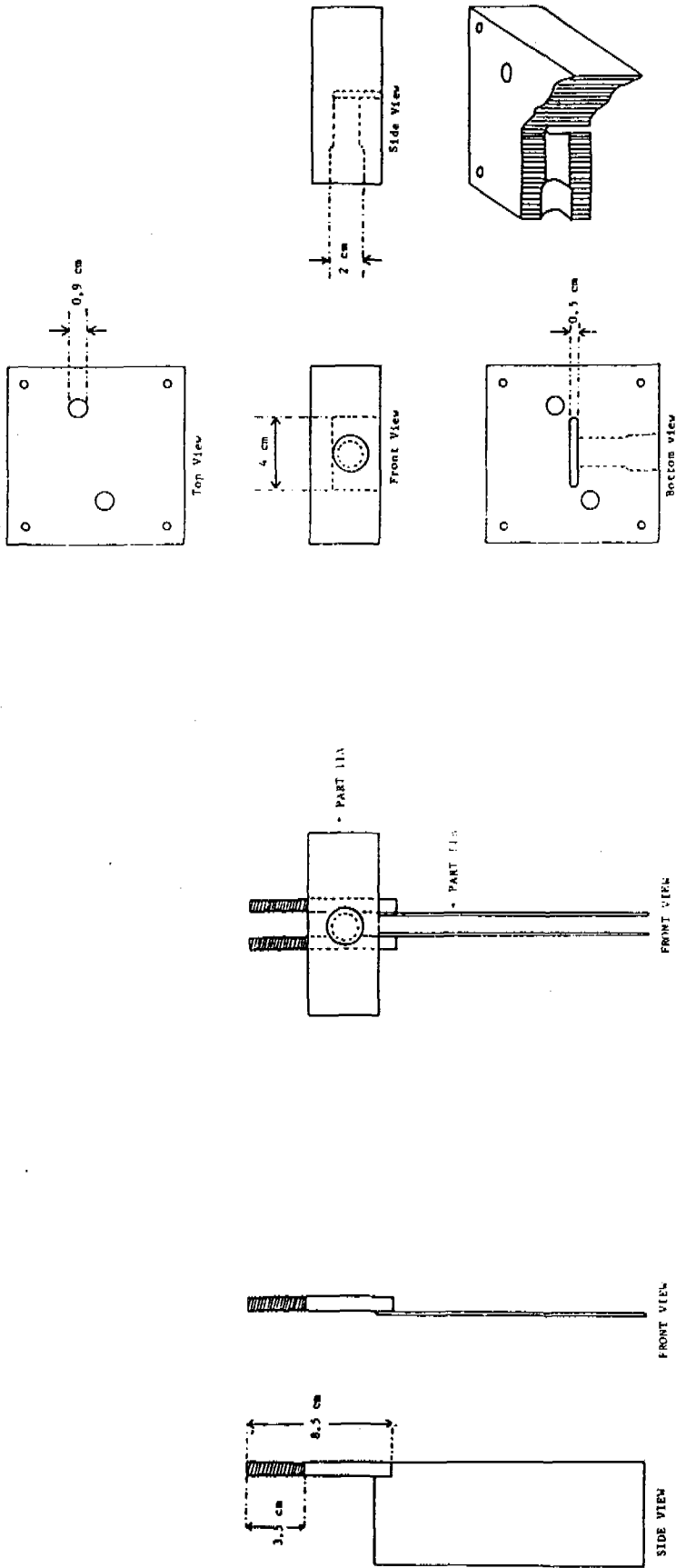


Figure 2-2: Hypochlorite Cell - Part I



Detail of Part IIB

Detail of Part IIA

Figure 2-3: Hypochlorite Cell - Part II

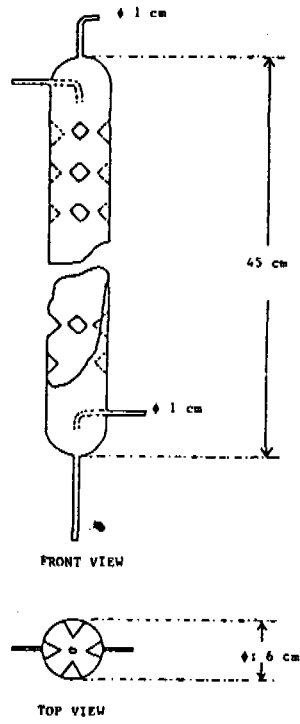


Figure 3: Gas separator

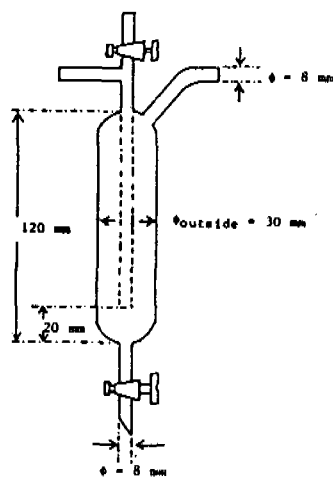


Figure 4: Cl₂ Absorber

APPENDIX

B. BIAMPEROMETRIC DETERMINATION OF HYPOCHLORITE,
CHLORITE AND CHLORATE.

1. Apparatus

Besides general analytical apparatus, such as burette, beaker etc. the following equipments are needed:

a. Stirrer

- Function : to stirr the solution during titration
- Quantity : one
- Type : magnetic stirrer
- Rating : rpm > 300

b. Modified ammeter

- Function : to indicate the end point of titration
- Quantity : one
- Type : DC-micro ammeter coupled with an amplifier
- Capacity : 25 microamperes

Amplifier circuit:

The circuit of the amplifier is given in the following diagram.

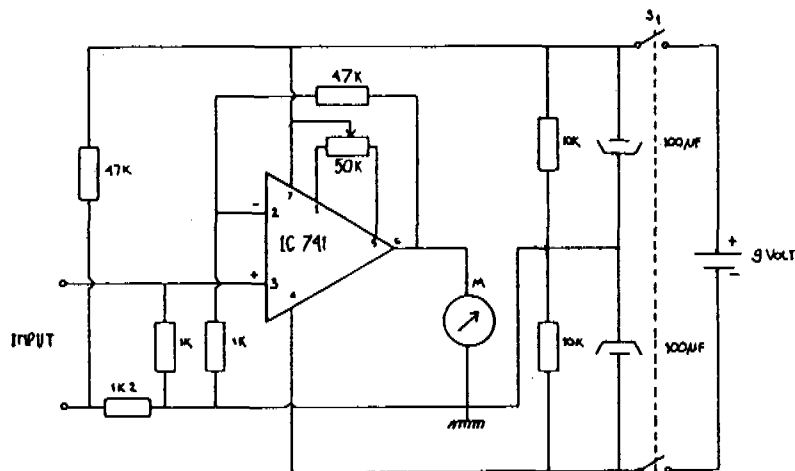


Figure 6: Diagram of Amplifier circuit

c. Electrode

Function : as the sensor for the end point of the titration.

Quantity : one pair

Type : Platinum electrode

NOTE: The electrode consists of platinum wire inserted in a glass capillary tube.

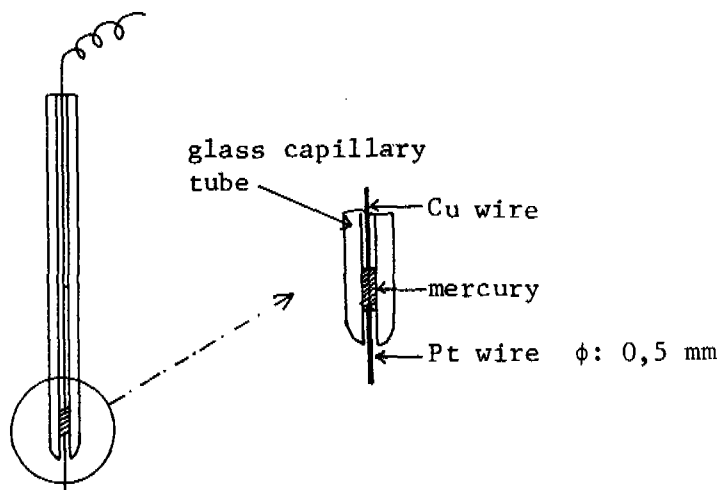


Figure 7: Pt-electrode

2. Reagents

a. Preparation of standard solution

0.05 M Chloramine-T solution:

Dissolve 14.1 g of chloramine-T, $\text{CH}_3\text{C}_6\text{H}_4\text{NC1Na}\cdot 3\text{H}_2\text{O}$ in 1 litre of water. This solution is standardized by arsenic(III) oxide.

0.05 M Arsenic(III) oxide solution:

Dissolve 2.5 g of arsenic(III) oxide in 20 ml of 1 M NaOH. Neutralize the solution with 2 M sulfuric acid to pH 6-7, and dilute it to 500 ml.

Phosphate buffer solution , pH 7:

Dissolve 7.12 g of $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ in 600 ml of water. Dissolve 9.07 g of KH_2PO_4 in 1 litre of water. Mix both solutions. In place of this preparation, Merck Puffer Titrisol 9887 can be used.

b. List of other chemicals

Sodium hydrogencarbonate, NaHCO_3 , p.a.

Potassium iodide, KI, p.a.

Potassium bromide, KBr, p.a.

Sulfuric acid, H_2SO_4 , 2M solution in water, p.a.

Hydrochloric acid, HCl, 12M solution in water, p.a.

Sodium hydroxide, NaOH, 4M solution in water, p.a.

3. Analytical Procedure

3.1. Sampling

The sampling procedure is applicable to diaphragm electrolysis brine containing not more than 75 meq. of chlorine-oxygen components per litre. Pipette 50 ml of the 0.05 M arsenic(III) oxide solution into a 250 ml volumetric flask. Add 25 ml of phosphate buffer solution pH 7 and transfer the sodium chloride brine sample (= a gram) into the flask. The sampling tube should be as short as possible and emerge into the arsenite-phosphate buffer mixture in order to avoid the loss of free chlorine. Allow to cool and fill up to the mark with water (= brine-arsenite mixture).

3.2. Determination of Free Chlorine + Hypochlorite

Pipette 25 ml of the brine-arsenite mixture into a 250 ml beaker, dilute to 100 ml with water, add 2 g of sodium hydrogencarbonate and dissolve. Add 2 g of potassium iodide, dissolve and titrate with 0.05 M chloramine-T solution. Determine the amount of titrant needed to the equivalence point (= V_1 ml).

3.3. Determination of Free Chlorine + Hypochlorite + Chlorite

Transfer to a 250 ml beaker 75 ml of water. Add 2 g of potassium iodide and dissolve. Add 15 ml of 2 M sulphuric acid. Pipette 25 ml of the brine-arsenite mixture into the beaker. Slowly add sodium hydroxide till the iodine just disappears. Add 2 g of sodium hydrogen carbonate and dissolve. Titrate with the 0.05 M chloramine-T solution. Determine the amount of titrant needed to the equivalence point (= V_2 ml).

3.4. Determination of Free Chlorine + Hypochlorite + Chlorite + Chlorate

Pipette 25 ml of the brine-arsenite mixture into a 250 ml beaker. Dilute to 100 ml with water. Add 2 g of potassium bromide and dissolve. Add 15 ml of 12 M hydrochloric acid and some anti-bumping granules. Heat and keep the solution boiling during 2 min, cool and titrate with 0.05 M chloramine-T solution. Determine the amount of titrant needed to the equivalence point (= V_3 ml).

3.5. Determination of the Blanks

Run a blank determination according to the procedure 3.2, 3.3, and 3.4 (= V_0 ml). Mix for these blanks 50 ml of the 0.05 M arsenic(III) oxide

solution and 25 ml of the phosphate buffer solution pH 7 and make up to 250 ml in a volumetric flask. In most times the blank values are virtually identical. If not, a correction has to be made for the deviation of the blank values in each titration.

5.6. Calculation

The sample contains:

$$\frac{(V_0 - V_1) \times m \times 2 \times 74.5 \times 10 \times 1000}{2 \times g} \text{ ppm NaClO}$$

(free chlorine included)

$$\frac{(V_1 - V_2) \times m \times 2 \times 90.5 \times 10 \times 1000}{4 \times g} \text{ ppm NaClO}_2$$

$$\frac{(V_2 - V_3) \times m \times 2 \times 106.5 \times 10 \times 1000}{6 \times g} \text{ ppm NaClO}_3$$

where:

m = molarity of the chloramine-T solution

g = mass of the sample

V_0 = ml of chloramine-T for the blank (titration 3.5)

V_1 = ml of chloramine-T for Cl_2 + NaClO (titration 3.2)

V_2 = ml of chloramine-T for Cl_2 + NaClO + NaClO₂ (titration 3.3)

V_3 = ml of chloramine-T for Cl_2 + NaClO + NaClO₂ + NaClO₃ (titration 3.4)

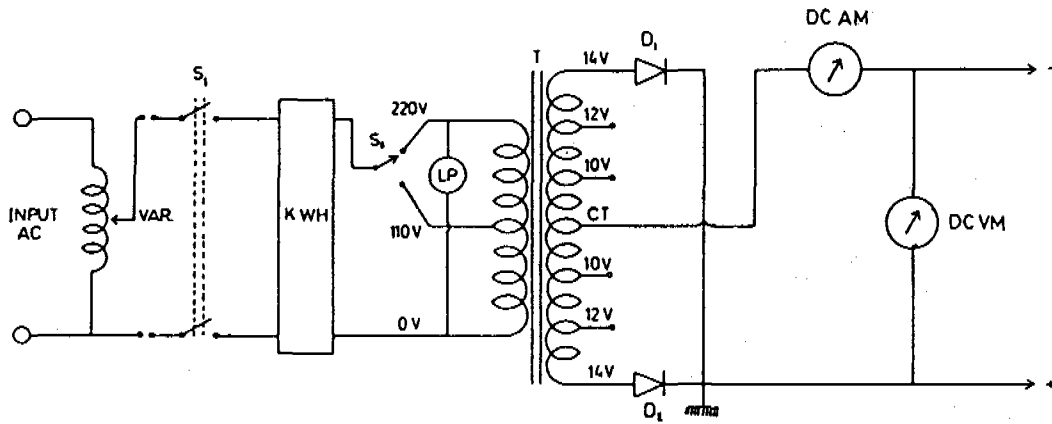


Figure 5: Direct current power supply unit

Legend:

- VAR : Variac
- KWH : Kwhmeter
- S₁ : Toglel switch
- S₂ : Slide switch
- T : Transformer 40 A
- D₁ : Diode 20 A
- D₂ : Diode 20 A
- DC.AM : Ammeter DC 0-50 A
- DC.VM : Voltmeter DC 0-30 v
- LP : Indicator lamp 220 V

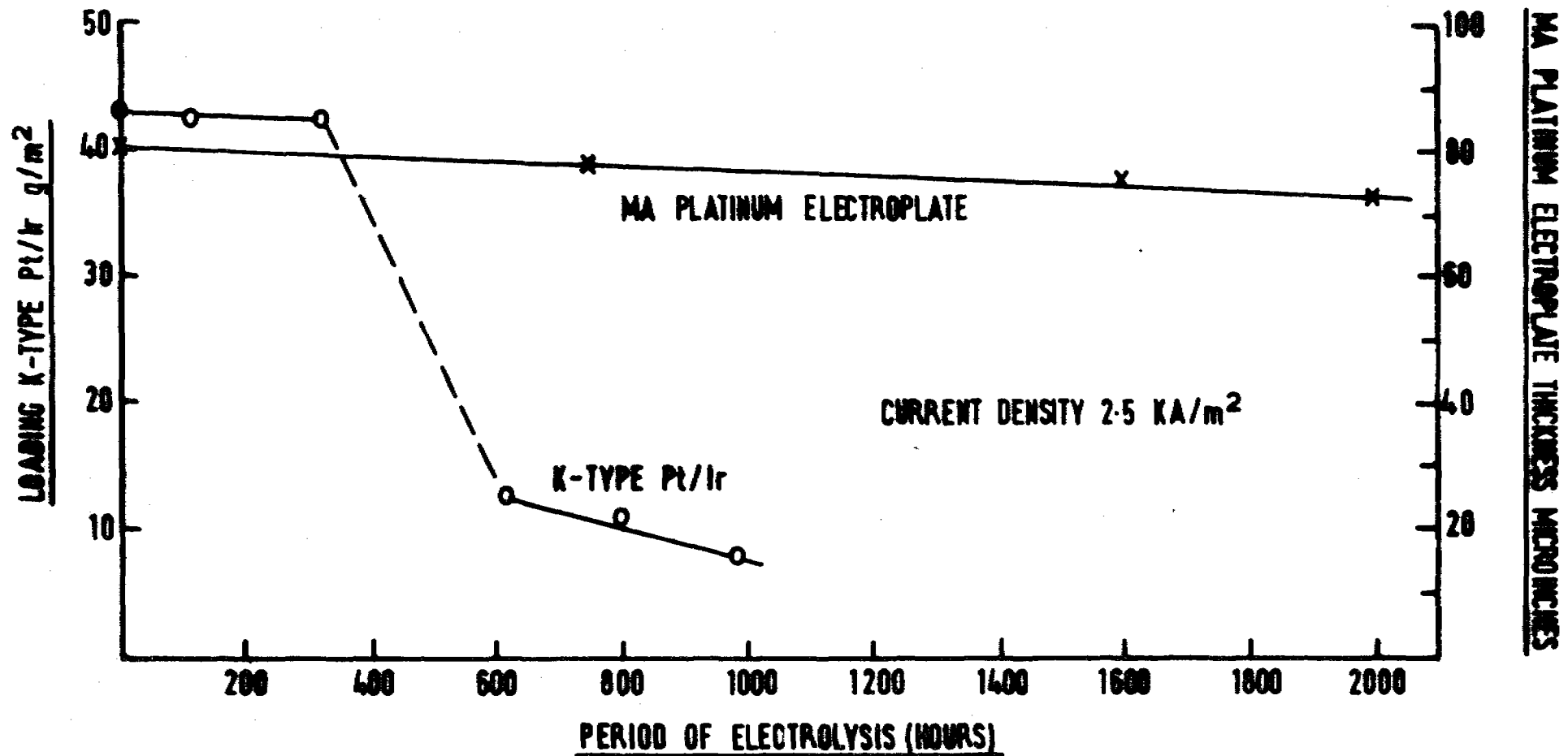


FIG. 8. CORROSION RATE OF MA PLATINUM ELECTROPLATE AND K-TYPE Pt/Ir COATED TITANIUM ANODES IN THE ELECTROCHLORINATION OF 3% SODIUM CHLORIDE AT 5°C

from Richards et al. Analytical Chemistry - 1957 Conf. on local functions

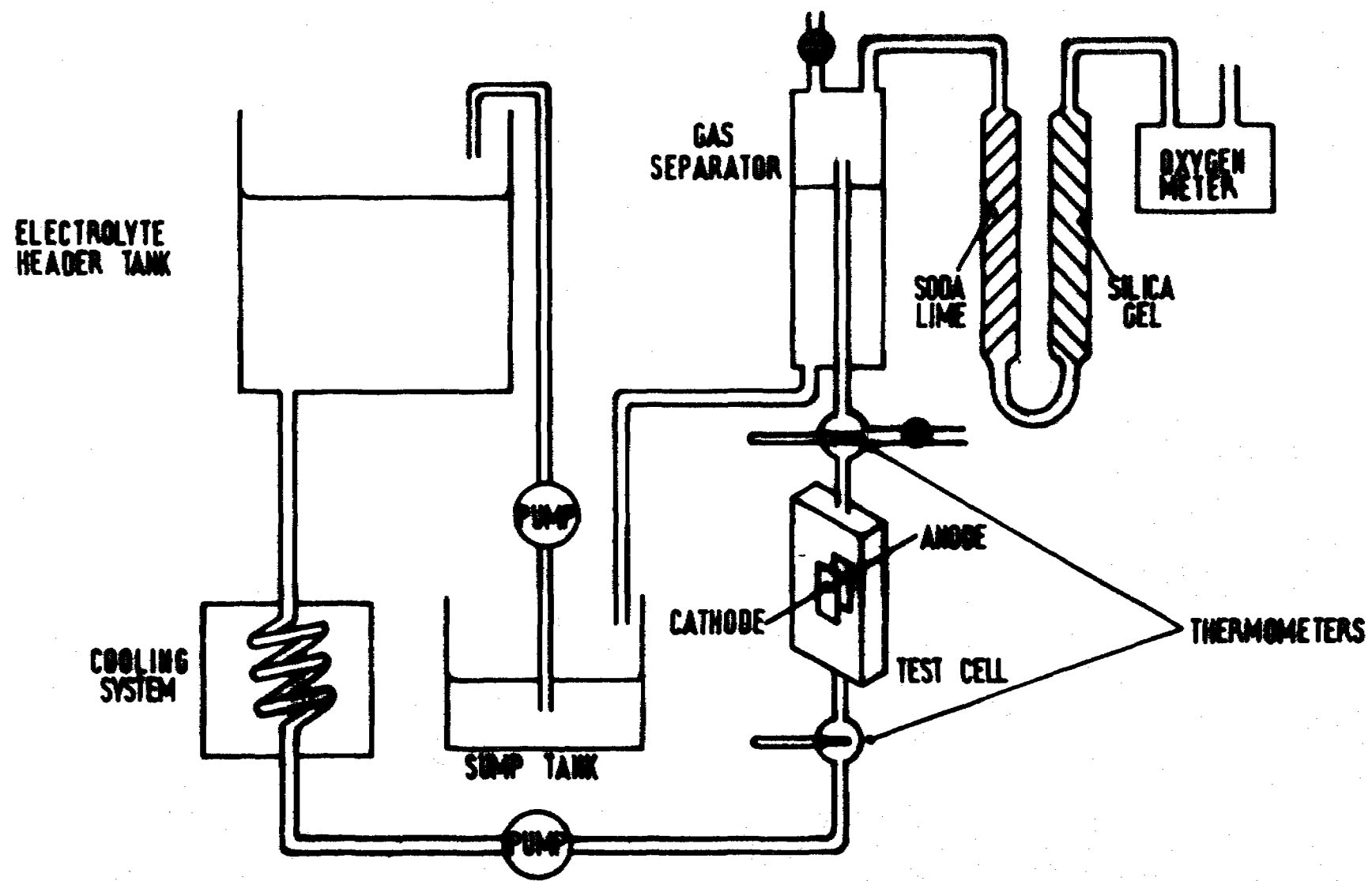


FIG. 7. LAYOUT OF LABORATORY HYPOCHLORITE TEST CELL