TARANTO DESALINATION PLANT: A COMPARISON BETWEEN THEORETICAL AND ACTUAL pH VALUES IN A CORRECT DESIGNED ACID TREATMENT PLANT

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ABSTRACT

The problem to increase the reliability of the acid treatment plants was tackled by ITALIMPIANTI with satisfactorily results in three steps:

1) By a theoretical calculation of the pH optimum distribution through the plant.

   This calculation has been performed adopting the accepted theory of CO_2 hydrolisis and HCO_3^- equilibria in sea water. Also practical values in the Debye-Huckel equation are used in worked examples.

2) By a correct positioning of chemical injection points and pH meters arrangement as illustrated in the P&I diagram.

3) By a correct sizing of decarbonating tower and degasifier which play a key rule in the success of acid treatment.

   This philosophy was applied in the 5th Desalination Plant which ITALIMPIANTI designed, built and put into operation in April 1980 for ITALSIDER at TARANTO Steel Work.

   A correct design of the plant permitted to reach easily the contract performance guarantees.

   A brief description of the technical features of the plant, the main parameters and the guide concepts of an easy acid treatment design are reported together with the same operational data collected during last year showing the stability and reliability of the system.

INTRODUCTION

The 5th Taranto desalination plant, designed and built by ITALIMPIANTI for ITALSIDER is located at TARANTO STEEL WORK and consists of one M.S.F. unit having a desalted water capacity of 250 t/hr.

The T.B.T. of $104^{O}C$ and the low gain ratio (6:1) have been chosen to utilize the available quantity of low pressure steam coming from existing backpressure turbines.

The desalted water is delivered to the steam boiler plant of the same Steel work.

The plant is complete with steam pressure reducing station, two brine recycle pumps (one steam turbine driven and the stand-by pump complete with electrical motor) and with all relevant ancillaries.

Main characteristics of Taranto desalination plant are listed herebelow:

|	
Evaporator type	M.S.F. long-flow
Design capacity	250 t/hr
Max top brine temperature	$104^{O}C$
Number of stages of Recovery section	12
Number of stages of Reject section	4
Output gain ratio	6 kg distillate/kg steam
Desalted water purity	less than 1 ppm
Sea water design temperature	$28^{O}C$
Materials	
Tubes	Cu Ni 90/10
Tubes sheets	Cu Ni 90/10
Water boxes	Cu Ni 90/10
Shell	Carbon steel (only the first three stages S.S. AISI 316 L lined)

Some photographs of the plant are reported in fig.1

MAKE-UP TREATMENT

The sea water make-up treatment adopted was the acid one by sulphuric acid.

Large availability of sulphuric acid and its low cost were the main reasons which led to that choice and ITALIMPIANTI was asked to solve the problem of acid treatment reliability.

Acid process is based on the following main reactions which happen in the decarbonator after the sulphuric acid injection:

$$CO_3^= + 2H^+ \rightarrow CO_2\nearrow + H_2O$$

$$HCO_3^- + H^+ \rightarrow CO_2\nearrow + H_2O$$
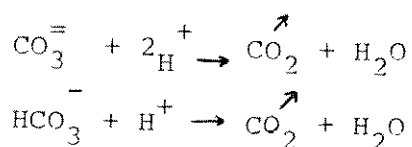
The concentration factor (recirculating brine/make-up ratio) kept in the TARANTO desalination plant is 1.6 against the value of 2.0 which could be adopted according to the calcium sulphate solubility limits.

After decarbonator, oxygen and CO_2 residual are stripped in a degasifier; sea water then enter the last stage to constitute the make-up.

The correct acid dosage is assured by the following control system:

- An hand control station that allows to fix the set point of the acid dosing rate (depending also on the sea water inlet alcalinity).
- A FRIC on the make-up stream that controls the right dosage of acid depending on make-up quantity.
- A pH meters controller after the mixer that adjusts the acid injected quantity depending on set point value of pH.

P&I diagram showing the process adopted is reported in fig.2.

Three principal features were taken into consideration because deemed responsible of success of acid treatment.

1) Good and immediate mixing of acid with make-up.
2) Reliability of pH meters
3) Oxygen removal and control

1) To match the requirements of a good mixing between sulphuric acid and sea water, a static mixer has been introduced just after the acid injection point.
   The static mixer, completely made of fiberglass, consists of a series of no-moving semielliptical plates positioned in a tubular housing.
   Due to complete turbulent type of flow and low viscosity of fluids to be mixed, a mixer containing 4 series of internal elements is sufficient to ensure a good mixing with head losses of about 5 m.w.c..
2) The pH meters installed utilize reference electrodes including Ag/Ag Cl halfcell which doesn't require electrolyte replenishment, external pressurization and ensures an exact value of pH measurement for a long time without reset and maintenance.
3) Finally oxygen removal is ensured by a vacuum degasifier with 3"1/2 Pall rings as packing.
   This tower was designed for an oxygen outlet stream content of 0.02 ppm using as stripping steam a small part of the steam produced in the 9th stage of distiller.
   Experience shows for this type of desorption (liquid film controlled process) that a minimum wetting rate of about 0.8÷1.0 m3/(hr x m) is a reasonable value which ensures a good and safe operation.
   Moreover some experiences carried out varying the steam/water ratio and measuring the oxygen content value in the outlet stream, led to conclusions that this ratio should be kept about 1 kg steam/ ton water to be degasified.

We can suppose the ionic strenght varies directly with sea water chlorosity according to the following relation:

$$I = 0.036 \times \left[Cl^- \right] \quad \text{(see APPENDIX A)}$$

Now introducing the Debye-Huckel law in relation (8) and (9) and solving with A = 0.53 that is a value valid for a water temperature of 40°C, we obtain:

$$pk_w^* = pk_w - \frac{0.2\sqrt{\left[Cl^- \right]}}{1+0.22 \sqrt{\left[Cl^- \right]}} \tag{11}$$

$$pk_1^* = (-pk_1) - \frac{0.2\sqrt{\left[Cl^- \right]}}{1+0.22 \sqrt{\left[Cl^- \right]}} \tag{12}$$

Where the variations of pk_w and $-pk_1$ with temperature can be represented from the following relations:

$$pk_w = 15.53 - 6.017 \; 10^{-2} \; T + 2.952 \; 10^{-4} \; T^2 \tag{13}$$

$$- pk_1 = 7.022 - 4.262 \; 10^{-2} \; T + 7.282 \; 10^{-4} \; T^2 - 3.642 \; 10^{-6} T^3$$

Values of a.m. relations are below resumed:

Temperature $^\circ$C	pk_w	$- pk_1$
30	13.98	6.30
40	13.60	6.249
50	13.26	5.256
60	12.98	6.299
90	12.50	6.43

Tab.1 pk_w and pk_1 values.

pH DISTRIBUTION THEORETICAL CALCULATION

Assumptions made for a correct acid dosage are as follows:
- Injection as much acid as required to neutralize almost the alcalinity M, leaving only 0.5÷1 ppm as alcalinity residual.
- CO_2 stripping efficiency in the decarbonator equal to 95%
- CO_2 content at outlet of degasifier equal to 0.1 p.p.m.
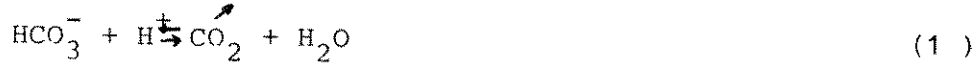- Sufficient pressure after acid injection to keep all CO_2 produced in solution.

With these hypothesis, with a sea water having the following chemical analysis:

Cl^-	20,500	p.p.m.
Na	11,000	p.p.m.
Ca	450	p.p.m.
Mg	1,500	p.p.m.
SO_4	3,000	p.p.m.
Alcalinity P	0	as p.p.m. $CaCO_3$
Alcalinity M	150	as p.p.m. $CaCO_3$

and at sea water make-up temperature of 40°C, applying previous equations we obtain the following figures:

pH THEORETICAL CALCULATION

Reactions involved in chemistry of desalination plants according to accepted theory are the following

$$HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O \tag{1}$$

$$CO_3^= + H^+ \rightleftharpoons HCO_3^- \tag{2}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3}$$

and the ionic balance is:

$$[H^+] + [Alk] = [HCO_3^-] + 2[CO_3^=] + [OH^-] \tag{4}$$

where [Alk] is the alcalinity residual expressed as equivalent/liter and then it represents the number of positive ions present in solution correlated to $[CO_3^=]$ and $[HCO_3^=]$ ions.

Hydrolisys of $[CO_3^=]$ is a linear combination of first three reactions.

Remembering that activities can be expressed as ionic concentration multiplied by activity coefficients, reactions (1) (2) and (3) give the following relations:

$$\frac{[CO_2]}{[H^+] \times \gamma_{H^+} \times [HCO_3^-] \times \gamma_{HCO_3^-}} = K_1 \tag{5}$$

$$\frac{[HCO_3^-] \times \gamma_{HCO_3^-}}{[CO_3^=] \times \gamma_{CO_3^=} \times [H^+] \times \gamma_{H^+}} = K_2 \tag{6}$$

$$[H^+] \times \gamma_{H^+} \times [OH^-] \times \gamma_{OH^-} = K_w \tag{7}$$

Substituting these relations in equation (4) and solving for $[H^+]$ we obtain:

$$[H^+] = \frac{-[Alk] + \sqrt{[Alk]^2 + 4\left[\dfrac{[CO_2]}{K_1 \, \gamma_{H^+} \times \gamma_{HCO_3^-}} + \dfrac{K_w}{\gamma_{H^+} \times \gamma_{OH^-}}\right]}}{2}$$

in which terms considered as infinitesimals are neglected.

If we put:

$$K_1^* = \frac{1}{K_1 \, \gamma_{H^+} \times \gamma_{HCO_3^-}} \tag{8}$$

$$K_w^* = \frac{K_w}{\gamma_{H^+} \times \gamma_{OH^-}} \tag{9}$$

we have at last:

$$[H^+] = \frac{-[Alk] + \sqrt{[Alk]^2 + 4\left(K_1^*[CO_2] + K_w^*\right)}}{2} \tag{10}$$

where the ionic quantity are expressed in gr.mole/liter.

after acid injection   pH = 4.2 ÷ 4.3 (^)
after decarbonating tower   pH = 5 ÷ 5.1
after deareator   pH = 6.5 ÷ 6.7
after caustic injection   pH = 7.4 ÷ 7.7

(^)   close to methyl-orange titration final point.
    As can be easily seen pH before and after decarbonator is
strongly influenced by CO_2 content.
    For this reason a diagram showing the pH versus alcalinity at
different stripping tower efficiency is reported (fig.3).

EXPERIMENTAL DATA

    Start-up took place on April 1980 and from that time values of
pH (fig.4), oxygen (fig.5) and other process parameters are shown
(fig.6).

CONCLUSIONS

    Values of pH theoretically calculated and practically observed
agree satisfactorily and pH values before decarbonator after acid
injection seem to be stable.
    Acid dosing system controlled by pH after static mixer seems
to be more reliable than that having set point controlled by pH
meter located at decarbonator outlet.
    In plants like this in Taranto, in which sea water alcalinity
changes because of mixing of different sources of sea water feed-
ing, pH should be adjusted at least daily according to the actual
sea-water alcalinity.
    pH values registered and oxygen contents analysis showed that
also decarbonator and deareator run properly and are well sized,
proving that both equipments play an essential rule in acid treat-
ment success.
    However if air leakages into the evaporators (by manholes,
local instruments joints, etc.) increase, it should be a good
practice to inject sulphite on the make-up to reduce the oxygen
content in the evaporator.
    In this case the chemicals injection points should be:
    acid   : no changes
    sulphite   : after deareator (instead of caustic soda)
    caustic soda : after the brine heater

    The sulphite infact has a good oxygen removal efficiency only at
low pH values.

LEGEND OF SYMBOLS

$[H^+]$	= hydrogen ion concentration	q ions/lt
$[Alk]$	= residual alcalinity	q equiv/lt
$[HCO_3^-]$	= HCO_3^- ion concentration	
$[CO_3^=]$	= $CO_3^=$ ion concentration	
$[OH^-]$	= OH^- ion concentration	
γ_i	= activity coefficient of component i	
K_j	= dissociation constant of reaction j	
pk_j	= log K_j	
I	= ionic strenght	
Cl^-	= chlorosity (gr/lt)	
z_i	= ionic charge of component i	
m_i	= molality of component i	
a	= mean diameter of ion	
T	= temperature $^\circ C$	

APPENDIX A

Debye Hückel law

Ionic strenght I for solution in which density of solvent is = 1 is expressed as follows:

$$I = \frac{1}{2} \sum z_i^2 \, m_i$$

in which z_i are ionic charge and m_i it is molality (or molality for our purposes).

Extended Debye-Huckel law has the following expression:

$$\log \gamma = - \frac{A \, z_i^2 \times \sqrt{I}}{1 + Ba \times \sqrt{I}}$$

in which:

a = is the mean diameter of a ion assumed as $3.5 \, 10^{-8}$ cm
B = is a coefficient which changes slightly with temperature and can be assumed equal to $.33 \, 10^8$.
A = is a coefficient which depends on the temperature according to the following table:

T $^{\circ}$C	A
25	.5117
90	.5920
110	.6265

APPENDIX B

Calculations example

pH calculation at decarbonator inlet

Sea water characteristics:
Alcalinity $= 150$ p.p.m. as $CACO_3 = 3.10^3$ g.ions/lt
Make-up temperature $= 40^{O}C$
Make-up chlorosity $= 20.5$ gr/lt
Residual alcalinity after acid injection $= .5$ p.p.m. as $CaCO_3 = 1.10^{-5}$ g.ions/lt.

pk_w $(40^{O}C) = 13.6$ from relation 13

$- pk_1$ $(40^{O}C) = 6.25$ " " 14

$pk_w^* = 13.6 - \dfrac{0.2 \times \sqrt{20.5}}{1 + 0.22 \times \sqrt{20.5}} = 13.15$ from relation 11

$pk_1^* = 6.25 - \dfrac{0.2 \times \sqrt{20.5}}{1 + 0.22 \times \sqrt{20.5}} = 5.8$ " " 12

$k_w^* = 7.14 \ 10^{-14}$

$k_1^* = 1.595 \ 10^{-6}$

CO_2 dissolved in make-up sea water generated from acid reaction is:

$$\dfrac{150 - .5}{50} \ 10^{-3} = 2.99 \ 10^{-3}$$

$$\left[H^+\right] = \dfrac{-1.10^{-5} + \sqrt{(1.10^{-5})^2 + 4 \ (1.595 \ 10^{-6} \times 2.99 10^{-3} + 7.14 \ 10^{-14})}}{2}$$

$= 6.31 \ 10^{-5}$ g.ions/lt from relation 10

pH $= 4.2$

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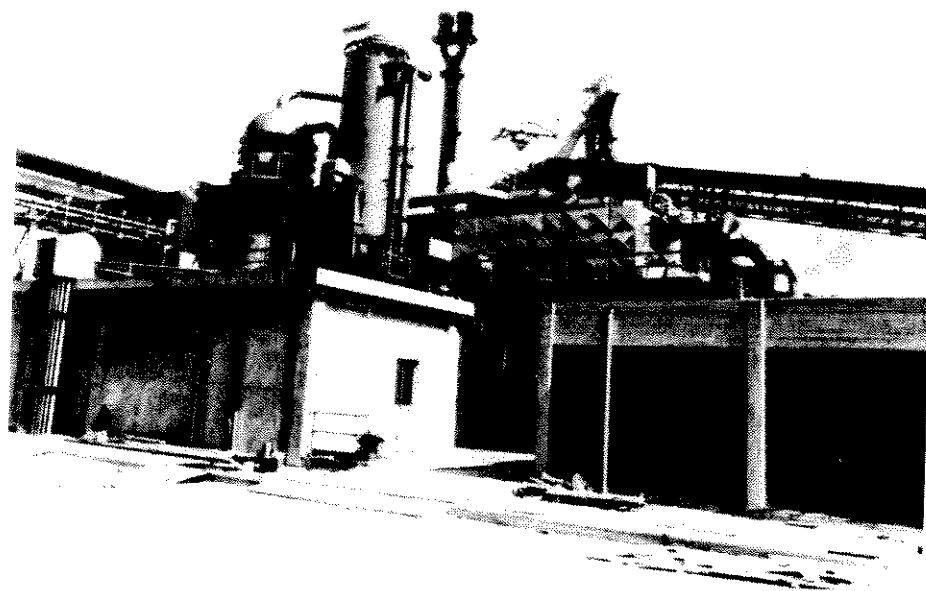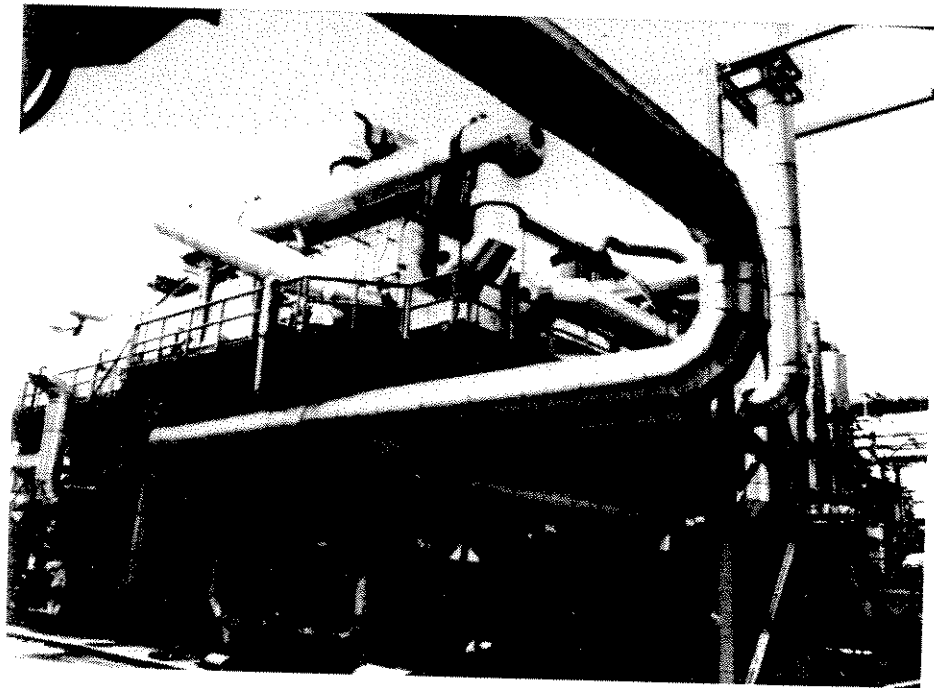
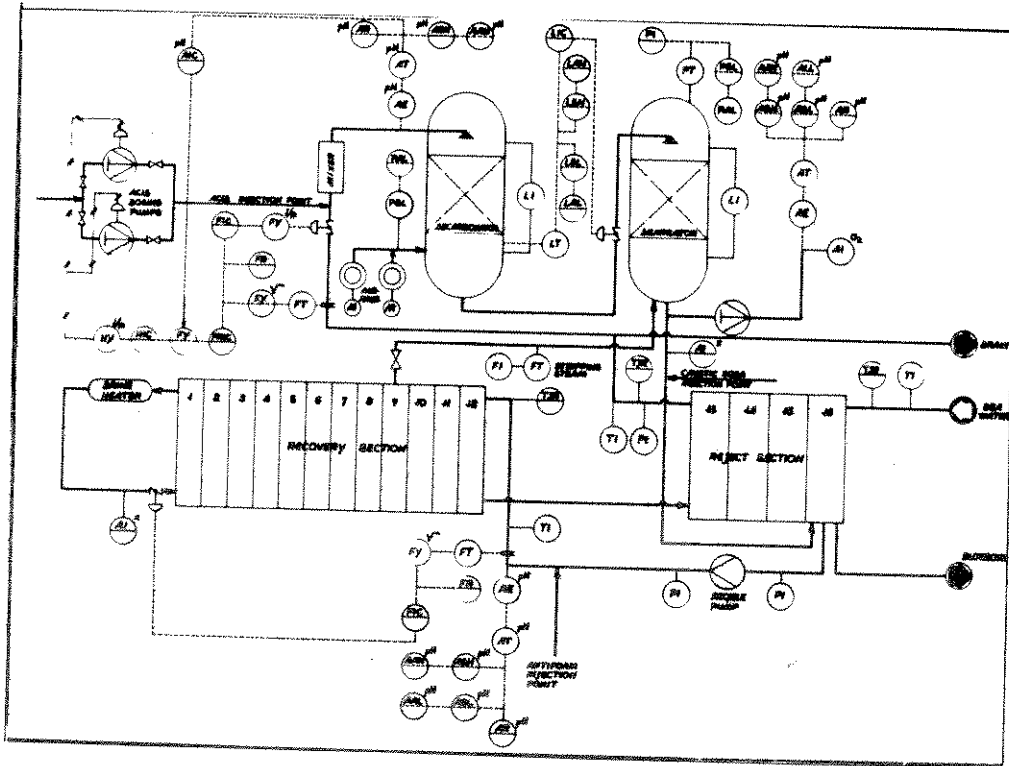Fig. 1 Taranto Desalination Plant:general views

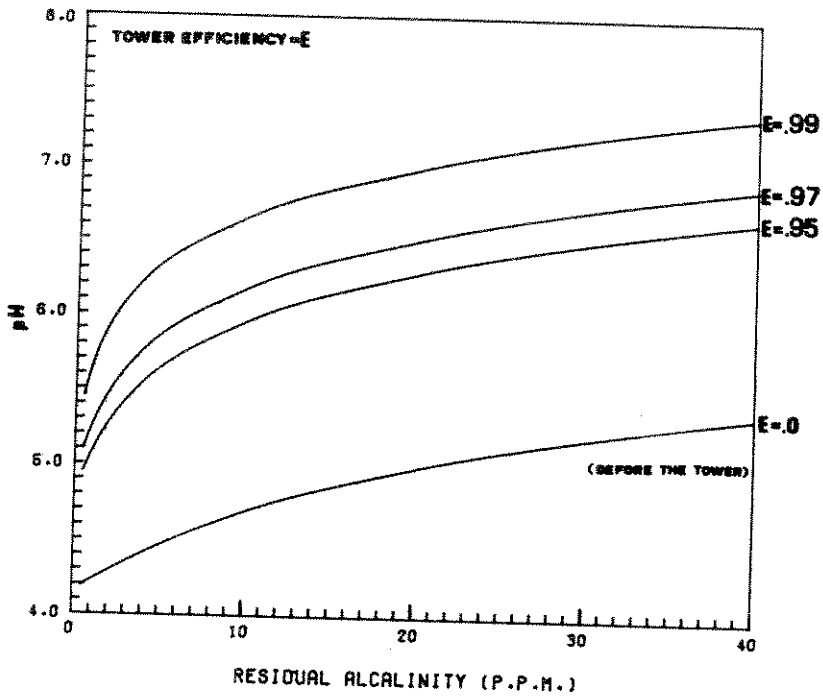Fig. 2   P & I diagram

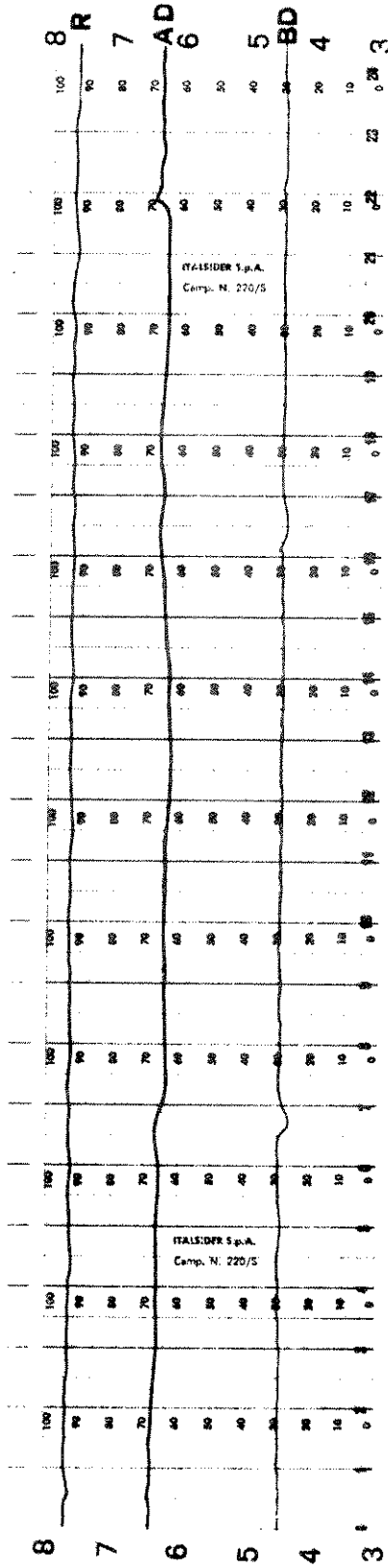Fig. 3 pH versus residual alcalinity for different
decarbonator efficiency

pH

Fig. 4 pH recorded data

R=recycle

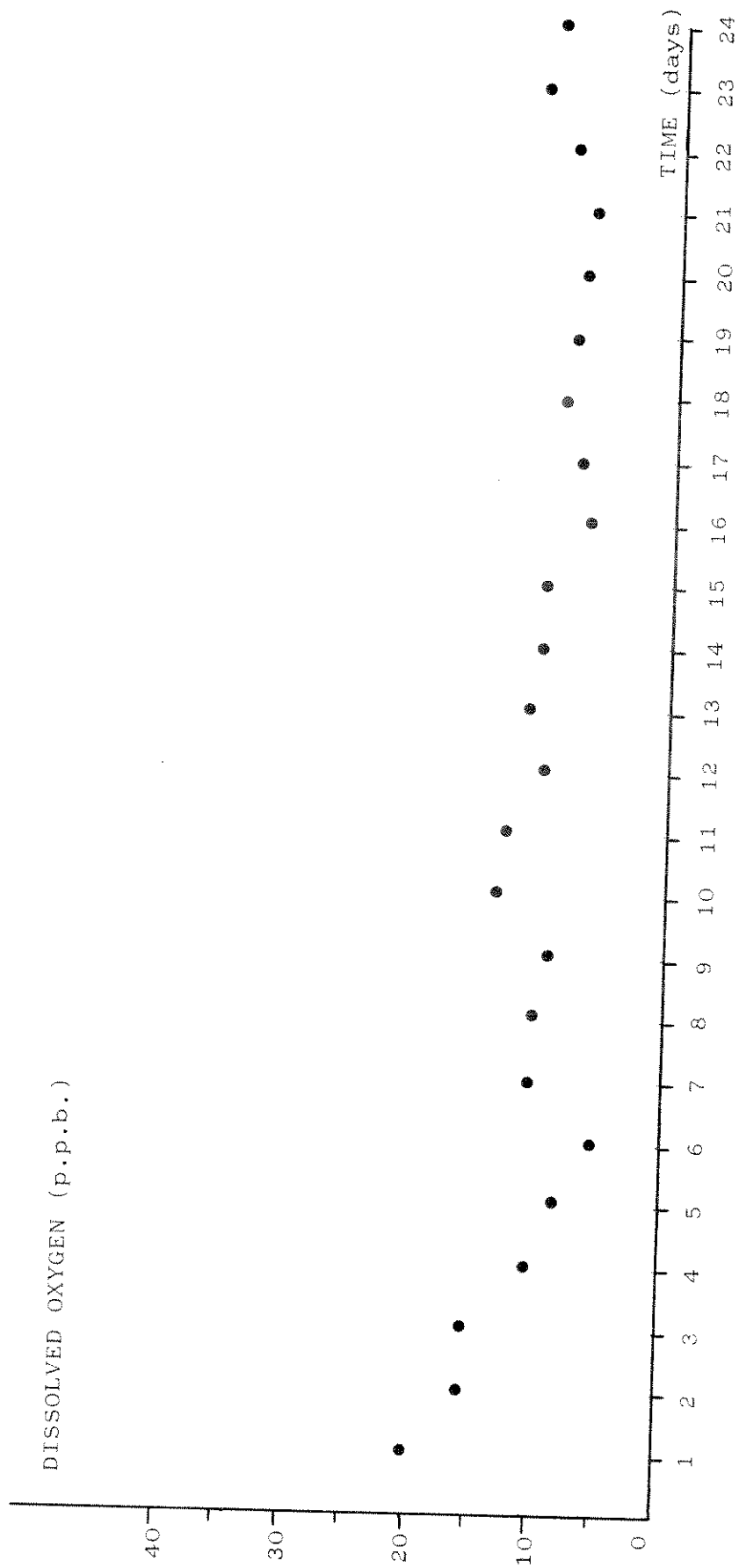BD=before decarbonator

AD=after degasifier

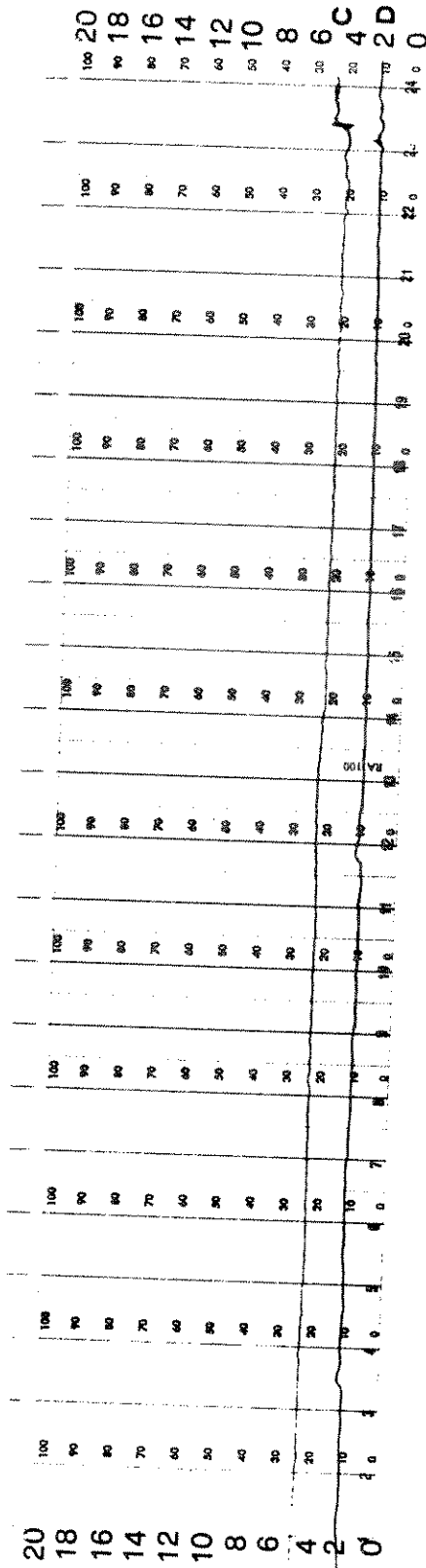Fig. 5 D.O. content in the make-up from deareator (start-up data)

Fig.6 Conductivity recorded data

D=distillate

C=condensate from Brine Heater