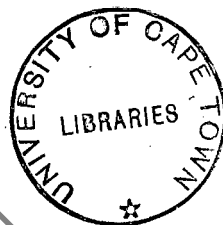AN INVESTIGATION OF TREATMENT

METHODS FOR HIGHLY MINERALISED

AND FLUORIDE BEARING WATERS

IN SOUTH AFRICA

A Thesis

Presented to the University of Cape Town

for the Degree of

Doctor of Philosophy

in the Faculty of Engineering

by

Gabriel Gideon Cillie B.Sc. (App. & Ind. Chem.)

CAPE TOWN
1956

SUMMARY

1. The demineralisation of saline water is receiving an increasing amount of attention all over the world.

2. In South Africa, fresh water supplies are limited and at present saline waters containing more than 2,500 p.p.m. of dissolved salts are being used by at least 150 communities and numerous individual farms, with possible deleterious effects upon the health of men and beasts.

3. Waters containing harmful concentrations of fluoride ($\geqslant 1.5$ p.p.m.) are also being used extensively due to the unsuitability of existing defluoridation methods.

4. Various methods of demineralisation and defluoridation were critically reveiwed, especially with regard to cost and practical feasibility. Most of them were found unsuitable for South African requirements which are:
   (a) a process for demineralisation of excessively saline water in small quantities, say 2 to 5 gallons per day, and
   (b) a process for defluoridation of fluoride bearing water in quantities from 5 to 5000 gallons per day.

5. In South Africa, demineralisation by means of solar distillation is attractive because plenty of sunshine is available in the many arid regions where small household supplies only, are required.

6. A programme of research was undertaken with an experimental solar still of 16 sq.ft. pan area, in order to correlate distillation efficiency with local climatic conditions.

7. An average daily yield of 6.762 Imp. gallons was obtained, equivalent to a 30% utilisation of the solar radiation impinging on the still.

8. Ambient and saline water temperatures were found to have an important bearing upon the efficiency of distillation. This observation has apparently not received the attention of workers elsewhere.

9. An equation, based on experimental data, was formulated to relate the thermal efficiency of the still with atmospheric temperature.

10. The influence of winds, rain, humidity and presure was mainly indirect as manifested in temperature and radiation changes.

11. Improved distillation was obtained from the use of mirrors and artificial cooling of condenser surface but their cost does not appear to be warranted.

12. Sufficient data was obtained to indicate a suitable design of household still and to estimate costs.

13. The efficiency of various methods of defluoridation were assessed. For this purpose the numerous methods of fluoride determination in water, were critically reviewed.

14. The method described by Stevens was found most suitable for direct routine estimation of fluoride ion concentration, while the standard distillation method was used as an intermittent check on the former method.

15. Flocculent precipitates will absorb fluoride from water, but the removal was found to be incomplete and impracticable.

16. Precipitated calcium phosphates were excellent defluori-
    dants but several disadvantages rendered them unsuita-
    ble for practical application in columns. They were
    also relatively expensive.

17. A cheap and efficient defluoridant was prepared by sim-
    ple treatment of superphosphate of lime with excess
    dilute sodium hydroxide solution.

18. Such activated superphosphate consists chiefly of micro-
    crystalline apatite which exchanges hydroxide ion se-
    lectively for fluoride ion. The exchange appears to
    be effected only on the surface of the crystals.

19. Granules of activated superphosphate were used success-
    fully in conventional ion exchange type filters for
    defluoridation of fluoride bearing water. The average
    defluoridising capacity of the material was 3.5 mg. F
    per gram taken within the range of fluoride reduction
    to the optimum limit, i.e. less than 1 p.p.m.

20. The ion exchange properties of the defluoridant are cri-
    tically controlled by changes in pH value. At pH values
    above 12 fluoride ions are exchanged for hydroxyl ions
    and at pH values between 6 and 8 defluoridation of water
    in contact with it proceeds rapidly.

21. After saturation with fluoride ions, the defluoridant may
    be regenerated with a 1% solution of sodium hydroxide.
    The method of regeneration which was developed restores
    the fluoride capacity of the material and no defluoridi-
    sed water is required for rinsing.
    A considerable saving of defluoridised water is thus
    attained.

22. Extensive tests were carried out on a pilot-scale defluori-
    dation filter column. The mechanism of regeneration
    was thoroughly studied and an optimum mode of operation
    was developed. It was found that efficient defluoridation
    could be maintained over a large number of defluoridation
    and regeneration cycles.

23. The defluoridant granules suffered some attrition loss
    during regeneration, but it was found to be no more severe
    than the attrition losses incurred by some commercial ion
    exchange media.

24. It was found that much harder granules could be obtained
    from a partially neutralised, granular superphosphate
    which recently (1954) became available in South Africa.
    The defluoridising capacity of this material was somewhat
    smaller than that of the previous media, but its greater
    mechanical strength rendered it a superior defluoridant.

25. The latter material was used in a large-scale defluoridation
    plant, designed by the author for the South African De-
    partment of Public Works. The plant has been operated
    independently, by the latter Department since January,1956.

26. For small-scale defluoridation, the use of powdered defluo-
    ridants, also prepared from commercial superphosphates,
    is recommended. Such powder or pulp should be added to
    a predetermined quantity of water and allowed to settle,
    after which the water will be potable.

27.   Patent cover for the manufacture and use of activated superphosphate defluridants has been obtained.

28.   Estimates of cost, indicated that defluoridation of both household and public water supplies by means of activated superphosphate should be a practical feasibility.

29.   The present investigations, have thus provided practical means for rendering both saline and fluoridised waters potable.

A N   I N V E S T I C A T I O N   O F   T R E A T M E N T

M E T H O D S   F O R   H I G H L Y   M I N E R A L I S E D

A N D   F L U O R I D E   B E A R I N G   W A T E R S

I N   S O U T H   A F R I C A

A Thesis

Presented to the University of Cape Town

for the Degree of

Doctor of Philosophy

in the Faculty of Engineering

by

Gabriel Gideon Cillie   B.Sc. (App. & Ind.Chem.)

PAARL
1956

CONTENTS PAGE

LIST OF FIGURES

INTRODUCTION.

By far the largest portion of the waters of the globe is unfit for human consumption, agricultural or process use, on account of excessive salt content. Up to the present time, natural fresh water supplies have been sufficient to meet most important needs, and development has been concentrated in areas where fresh water supplies are plentiful. Continuous expansion, however, has accelerated the need for additional water resources such as may be obtained from demineralisation of saline waters.

In South Africa water supplies are limited and the need for demineralisation is consequently urgent.

Whereas the removal of organic impurities from water has already become established practice, economic demineralisation has not been attained as yet. Due to the difficulty and cost of total demineralisation, methods for removal of a specific harmful ingredient only are often resorted to. One such ingredient which often occurs in natural waters and which must not exceed a concentration of 1.5 parts per million (p.p.m.) in potable water, is fluoride ion. Up to the time of the present investigation, no practical method of defluoridation had been applied.

As a result of these imperfections many parts of South Africa, and in particular the West coast and South West Africa, have suffered the ill-effects of a fresh water shortage.(1)! The development of these and other regions has been severely handicapped but their valuable resources and potential value to the country as a whole, call for serious consideration of the problem. The present investigations were undertaken in order to clarify existing conditions and to develop economic means for rendering saline waters potable. It was further attempted to develop a practical method for defluoridation of waters which contain fluoride ion only, in excessive concentration.

After careful review of various methods of demineral-
isation, it was decided to concentrate attention on the production
of fresh water by artificial solar distillation. It was found
that a relatively small experimental solar still could produce an
annual average of 0.762 Imp. gallons of distilled water per day.
The yield of distillate was mainly determined by the amount of
radiation received by the still, but the influence of other
climatic factors was also evaluated. From the data presented it
is possible to design a still which will under South African
conditions provide a specified quantity of distilled water. Such
a solar still may be constructed for, or by individual house-
holders at reasonable cost and will thereafter operate carefree and
costless.

Defluoridation of water was accomplished with an ion-
exchange material which was prepared from a cheap and readily
available raw material viz. commercial superphosphate of lime.
The active ingredient of the preparation was found to be micro-
crystalline apatite which reversibly and selectively exchanges
fluoride and hydroxide ions. After saturation with fluoride ions
the material could thus be regenerated successfully with a dilute
solution of sodium hydroxide. It was found that pH control
during defluoridation and regeneration was of primary importance,
an observation which had not been evaluated before.

Details of practical defluoridation are presented so
that the process should be amenable to interested parties.

The investigations were carried out in the Water Research
Laboratory of the South African Council for Scientific and
Industrial Research and occupied a period of four years, from 1950
till 1954. Papers on Water Quality Requirements, Defluoridation
and Solar Distillation were published in various journals and
C.S.IR. Reports. (See appended list of publications.) These papers
constitute the main subject matter of this thesis.

CHAPTER I

THE OCCURRENCE AND DISADVANTAGES OF HIGHLY
MINERALISED AND FLUORIDE BEARING WATERS

I.   OCCURRENCE OF SALINE WATER.

      The unlimited supplies of water contained in the oceans are the most common example of saline waters which have remained unexploited.   In addition all underground waters contain varying amounts of dissolved mineral matter, as a result of their percolation through strata with more or less soluble mineral constituents.   The nature of underground waters is therefore dependent on the geological formations from which they arise.

      In high rainfall areas the soluble constituents of rocks are gradually leached out and depleted, resulting generally, in low salinity underground water.   In arid regions, the reverse takes place since rapid evaporation of ground water enriches the soluble minerals in the soil.   Unfortunately it is exactly these regions which have to rely most upon boreholes and wells for water supplies.

      During the course of the present studies, a survey was undertaken of the occurrence and physiological effects of saline water in South Africa.   The attached map (figure 1) was compiled from analysis of various domestic waters of which samples were submitted.   It was further supplemented by records of the Department of Public Health.   Waters which contained more than 1000 p.p.m. of dissolved salts only, were recorded since lower concentrations are within the specifications for potable waters (2).

      From figure 1 it is obvious that water with excessive salinity occurs in a large number of places in all parts of South Africa.

      Further information regarding the consumption of saline water was sought via questionaires which were sent to Town Clerks

B E C H U A N A L A N D

PORTUGUE

KALAHARI DESERT

EAST

S O U T H   W E S T

AFRIC

⊙KARIBIB

⊙PELICAN POINT

⊙LEKKERWATER

A F R I C A

⊙KALKRAND

⊙SALZBRUNN

⊙⊙MORAN

⊙⊙PIETERSBURG

⊙⊙POTGIETERSRUST

T R A N S V A A L

⊙PILANSBERG

⊙MAFILO

⊙BREYTEN

⊙ERMELO

SWAZI-
LAND

⊙⊙SEEHEIM

⊙⊙⊙⊙GORDONIA
⊙⊙⊙⊙

⊙GR.HAFWATER

⊙KALKFONTEIN
⊙HAMRIDER

⊙⊙UPINGTON

⊙WOLHUTERCA

⊙⊙KROONSTAD
⊙BLOEMHOF   ⊙⊙KROONSTAD
⊙⊙⊙HOOPSTAD ⊙ODENDAALSRUS
CHRISTIANA   ⊙LINDLEY

O R A N G E   F R E E

ATLANTIC

⊙ALEXANDER BAY

⊙BEACONSFIELD

S T A T E

⊙PELLA
⊙POFADDER

⊙⊙⊙⊙⊙⊙⊙⊙KENHARDT
⊙⊙⊙⊙⊙⊙⊙
⊙NAMIES

⊙PORT NOLLOTH

N A T A L

⊙LOWER TUGELA

⊙UMHLALI BEACH

O C E A N

⊙PRIESKA

⊙HOPETOWN

B A S U T O   L A N D

⊙RICHMOND

O C E A

⊙OTRANSBOK

⊙SCERATSFONTEIN
⊙⊙KAMIESAROON
⊙WOLFERVIAL

⊙VAN WYKS VLEI

⊙PHILIPSTOWN

⊙SPRINGFONTEIN

⊙⊙⊙GARIES

⊙BRANDVLEI

⊙⊙DE AAR
⊙BRAKRIVIER

⊙CARELUS
⊙⊙TONYDALE

⊙ALIWAL NORTH

⊙⊙IZANA

⊙LIEUWSFONTEIN

⊙MERRIMAN

⊙⊙BITTERFONTEIN
⊙NGWERHS   ⊙NIEUWOUDTVILLE   ⊙CALVINIA
⊙VAN RHYNSDORP

⊙⊙WILLISTON

⊙VICTORIA WEST

⊙UMTATA ⊙PORT ST JOHNS

C A P E   O F   G O O D   H O P E

⊙HOFMEYR

LEGEND

TOTAL DISSOLVED
SOLIDS (P.P.M.)

⊙CLANWILLIAM

⊙GRAAF REINET

⊙MORTIMER

1000–2000 ⊙	POTABLE
2000–3000 ◐	OBJECTIONABLE
3000–4000 ◑	REQUIRES ACCLIMATIZATION
4000–5000 ◕	INIMICAL TO HEALTH
>5000 ●	DANGEROUS

⊙⊙ BEAUFORT WEST
⊙⊙LETSJESBOSCH

⊙⊙KENDREW

⊙⊙FORT BEAUFORT
⊙ SOMERSET EAST ⊙KROOMIN

⊙KROMFONTEIN
⊙PRINCE ALBERS RD

The circles represent individual boreholes, wells, or springs
in the districts named.

Waters containing less than 1000 ppm of total
dissolved solids are not recorded.

⊙⊙JANSENVILLE
⊙⊙KLIPPLAAT

⊙E KINGWILLIAMSTOWN
⊙EAST LONDON

⊙LAINGSBURG
⊙CONSTABLE
⊙HERMON ⊙TOWNS RIVER

⊙PRINCE ALBERT

⊙⊙⊙WILLOWMORE ⊙STEYTLERVILLE

⊙⊙ ALBANY ⊙PEDDIE

⊙ZUNEY ⊙BATHURST

Figure 1

UNION OF SOUTH AFRI

QUALITY OF UNDERGROUND
WATER SUPPLIES (SALINE)

⊙⊙WORCESTER

⊙⊙OUDTSHOORN

⊙HAMPER

⊙STELLENBOSCH

⊙COLDSTREAM

⊙UITENHAGE
⊙ALEXANDRIA

⊙⊙GAMTOOS R
⊙PORT ELIZABETH

⊙MOSSEL BAY

0 0 0   40   80   120
MILES

and Veterinarians in areas where saline waters are prevalent. The replies indicated that saline water is of necessity being used by a large number of people. Combined data indicate that water containing more than 2500 p.p.m. of dissolved salts (the maximum allowable salinity for potable water - see below) is used by at least 150 communities.

II. OCCURRENCE OF FLUORIDES IN WATER.

The occurrence of fluoride ion in ground water is dependent on the nature of the geological formations from which the water arises. Minerals such as fluorspar, fluorapatite, topaz and fluocerite all contain appreciable quantities of fluorine, while the various micas, amphiboles and tourmaline, etc. contain lesser amounts.

The occurrence of fluoride ion in water in South Africa is widespread (1) since nearly all geological formations contain fluorine. Ockerse (3) surveyed the incidence of fluoride in relation to endemic fluorosis and found that as many as 805 areas were affected. It was most prevalent in the following areas :-
Saltpan, Transvaal; Kalkheuvel, Transvaal; Pilansberg, Transvaal; Warmbaths, Transvaal; Kenhardt, C.P.; Gordonia, C.P.; Dewetsdorp, O.F.S. and Shannon, O.F.S. In these areas water containing up to 40 p.p.m. fluoride is used for domestic purposes. In addition nearly all the underground water resources of the north-western Cape, as well as South West Africa, contain varying quantities of fluoride.

III. DISADVANTAGES OF SALINE AND FLUORIDISED WATERS.

All salts in solution change the physical and chemical properties of water. Some salts may have deleterious physiological and toxic effects while others may be quite harmless, but they all

/have.....

have the common property of changing the osmotic pressure of water, the latter being of prime importance in all biological processes. Since specific uses allow for different tolerance limits, the objections to saline and fluoride bearing waters are best discussed in relation to the major beneficial uses of water viz., A. Domestic water supply, B. Industrial water supply and C. Agricultural water supply.

A.   Domestic Water Supply.   (Human consumption.)

Maximum permissible limits for the concentration in drinking water, of certain substances such as lead, arsenic, selenium, barium, etc., have been prescribed by the South African Bureau of Standards.(2).   The toxic effects of these substances are well-known and need no further elaboration.

The physiological effect of fluorides has only recently been clearly established, although mottled dental enamel had been noted and described as early as 1901 by Eager.(4).   Despite the intensive researches of several investigators, it was not until 1931 that mottled dental enamel was correctly attributed to fluorides, almost simultaneously by Churchill (5), Smith (6) and Velu (7). Since then the incidence of fluorides in drinking water has been the subject of much study.

From 1935 onward Dean et al, (8, 9, 10, 11, 12, 13) have reported that fluoride concentrations below 1.0 p.p.m. in drinking water produce no significant mottling.   Above this concentration, however, fluorides are harmful.   An important result of their work was the observation that the incidence of dental caries was considerably lower among children with mottled enamel than among those with no mottling.

Since then, the application of fluorides as a caries control measure has been studied extensively (14, 15, 16).   As a result many public water supplies in the United States of America

/are......

are at present enriched with fluorides to a mean concentration of approximately 1 p.p.m. (17, 18, 19). Preliminary reports indicate that a considerable decrease in caries rate has been attained among children below 12 years of age - the period during which the permanent teeth are being formed. The increased resistance to dental caries is carried over into later life to an appreciable degree.

In South Africa Ockerse (20) made similar observations in regard to the caries - mottled enamel relationship. The caries rate amongst children suffering from mottled enamel was 28 per cent compared with 69 per cent for normal children. It was also found that the fluoride content of teeth of low caries incidence was very much higher than that of teeth of high caries incidence.

The consumption of fluoride in excessive quantities may also adversely affect the entire bone structure (3) and there is evidence that it may be a causative factor in goitre (21, 22).

With regard to the consumption of water containing non-toxic salts such as $NaCl$, KCl, $MgSO_4$, $MgCl_2$, $CaCl_2$, etc., the implications are not very clear. Limits for the total dissolved solids concentration have been proposed (2) viz. 500 p.p.m. for class A water and 1000 p.p.m. for class B water, but considerable controversy and speculation still exist. The objections to high salt concentrations in potable water supplies are based on two factors, viz. taste and physiological effects.

(a)   Taste.

The presence of high salt concentrations in water is easily detected and the objectionable taste curtails consumption at levels which is generally well below that at which any serious physiological effects can be expected.

Several workers have studied the limits to which the palate can detect salts in water. Thus, Richter and Maclean (23)

/in.....

in a study of 53 adults, found that the median level of recognition
for sodium chloride in water was 650 p.p.m. The ability of a
limited number of observers to detect various mineral substances in
water was reported on,by Whipple (24) as follows :

Sodium chloride	detected at	200 - 450	p.p.m.
Potassium chloride	" "	350 - 600	"
Sodium sulphate	" "	250 - 500	".
Magnesium sulphate	" "	400 - 600	"
Magnesium chloride	" "	200 - 750	"
Calcium sulphate	" "	250 - 900	"
Calcium chloride	" "	150 - 350	"
Sodium nitrate	" "	450 - 800	"
Sodium carbonate	" "	15 - 75	"
Sodium and potassium hydroxide	" "	1 - 50	"
Calcium carbonate	" "	50 - 200	"

From these results it is apparent that neutral salts are
perceptible to the taste at concentrations of from 300 to 900 p.p.m.
and water generally becomes unpalatable at concentrations of 1,000
to 1,500 p.p.m. Alkalis such as sodium and potassium hydroxide and
sodium and calcium carbonate can be detected at lower levels and
would become objectionable at correspondingly lower concentrations.

The palatability of saline waters, however, will not
always restrict its use because it is well-known that acclimati-
sation of subjects using such water will reduce their ability to
detect the salinity. Physiological effects rather than taste
should thus receive priority in judging the suitability of a water
for domestic use.

(b) Physiological effects

As may be expected, the non-toxic neutral salts produce
major physiological effects only when ingested at concentrations
above their isotonic levels. At these concentrations they produce
dehydration of the body tissues and if ingestion is continued it will
result in death. For most neutral salts the isotonic concentrations
are between 6,000 and 8,000 p.p.m., but obviously such excessively
saline waters are rarely consumed, even in emergencies.

The effects of the consumption of water containing lower concentrations of these salts have been reported on by several investigators (25, 26, 27, 28). In South Africa the subject has been studied extensively by Steyn and Reinach (21). With regard to the permissible salinity of a domestic water, they agree with older authorities in England and America that the extreme limit of the total salt content should not exceed 570 p.p.m.

The consensus of opinion is that minor physiological effects such as gastric disturbances and catharsis may be caused by drinking of saline waters. These effects are particularly experienced by persons who have been accustomed to water of low salinity. However, no permanent damage is produced and tolerance for such water is soon acquired.

Magnesium, sulphate and phosphate ions are specially active in producing catharsis, but Sollman (25) states that below 1,000 p.p.m. they are harmless. MacDougal (26) found that water containing up to 2,500 p.p.m. of dissolved salts may be used for many days without serious discomfort. If the saline content is increased to 3,300 p.p.m., only hardened subjects may use it while 5,000 p.p.m. is inimical to health and comfort, though it might suffice for a few hours or save the life of a person who had been wholly without water. This suggests that the limit of tolerance for drinking waters could be raised above 1,000 p.p.m., perhaps even to the vicinity of 2,500 p.p.m. without adverse effects for those accustomed to them. The human body always protects itself against adverse conditions and any ill-effects caused by the drinking of saline waters are thus most likely to be of a chronic rather than acute nature.

It should be pointed out, however, that possible synergistic or antagonistic interactions between mixed salts in solution may cause different effects from those of the separate salts. In addition there are several other factors such as quantity of water

consumed,
/climatic conditions and individual resistance which will influence
tolerance limits. On the whole it may be taken that water, contain-
ing more than 2500 p.p.m. of dissolved solids should not be used for
drinking purposes.

B. Industrial Water Supplies.

The quality requirements of industrial water supplies are
of necessity varied, in that they depend on the use to which the
water will be put. With regard to dissolved solids content consider-
able tolerance is possible when the water is intended for washing and
similar purposes. On the other hand excessive dissolved solids can
cause foaming in boilers and interfere with clearness, colour and
taste of the finished products. It is therefore desirable that some
limits of salinity should be exercised.

In Table I some major industrial uses have been listed
together with suggested limiting concentrations of dissolved solids.
The figures are by no means rigid since their values depend largely
on individual circumstances. They do, however, indicate that
industries generally require water of lower salinity than is needed
for human consumption.

The presence of fluoride ion in the low concentration which
generally occur in water, will not interfere with industrial processes
with possibly two exceptions. The first is in cases where the water
is concentrated in a product intended for human consumption and the
second is in ice manufacture. Several reports have indicated that
fluoridation of water has rendered the ice made therefrom, more
brittle and consequently difficult to handle.

C. Agricultural Water Supplies.

High salinities of irrigation waters may be deleterious to
plants directly, or indirectly through their effects on the soil.
High concentrations of sodium are especially harmful in that it

TABLE I.

SALINITY LIMITS OF WATER FOR INDUSTRIAL AND AGRICULTURAL USE.

	Purpose	Maximum Salinity (p.p.m.)	Authority
I N D U S T R I A L	Food Processing	Domestic Standards	-
	Feed for boilers at $>$400 p.s.i.	50	Jour. N.E. Water Works Ass., 54, 261, (1940)
	Chemical Industries	Depends on product	-
	Cooling Water	Sufficiently low to prevent scale formation	-
	Textiles	200	Thomas, J.F.J., Water & Sew. Works, 86, 21 (1948)
	Plastics	200	"Water Quality and Treatment" 2nd. ed. Am. Water Works Ass., (1950)
	Pulp and Paper	500	Miller, L.B., Paper Trade Jour., TAPPI Sect.110 (1940)
	Steel	No limit	-
I R R I G A T I O N	Salt Sensitive Plants e.g. Fruit Trees and most Vegetables	500 to 1000	1. Chapman, H.D. et al., Report of Internal Comm. on Water Pollution, California State Assembly (1949)
	Plants with moderate tolerance e.g. cereals, lucern and perennial grass.	2000	2. Journ. of Agric. of Western Australia, 27, Series 2, 156, (1950)
	Salt Resistant Plants e.g. Wild grasses and sugar beet.	3000	3. "Water Quality Criteria" State of California Water Pollution Control Board, Publ. No.3 (1952)
S T O C K D R I N K I N G	Poultry	3000	1. "Water Quality Criteria" as above.
	Pigs	4000	2. Personal communication by Dr. W.C. Visser of the Agric. Research Lab., Utrecht, Holland, (1952)
	Horses	6500	
	Cattle	9000	
	Sheep	12000	3. Chebotarev, I.I., Water & Water Eng., 56, 132, (1952)

causes disintegration of soil granules with consequent low soil
porosity and permeability. It is not possible to fix absolute
limits for permissible concentrations of salts in irrigation
waters since their effects may be modified by a number of factors,
such as concentration of the solute in the soil due to evaporation,
character of the soil, drainage conditions, types of salt present,
the kind of crop, climate, etc. Some indication of the maximum
allowable salinities for irrigation of various plants is, however,
given in Table I. The figures are averages of the values quoted
by the authorities listed.

The quality requirements of water used for stock feeding
are far less exacting than for most other purposes as will be seen
from Table I. The figures quoted are again averages of the
various authorities listed.

Fluorides, in the concentrations normally found are
generally not as objectionable for animals or agricultural purposes
as for human consumption. Cattle may suffer from dental
fluorosis but they are generally slaughtered before severe
calcification and embrittlement of teeth and bone can occur.

IV. THE IMPLICATIONS OF IONIC CONTAMINATED WATERS
IN SOUTH AFRICA.

The low average rainfall of certain regions in South Africa,
necessitates dependence on underground water which is often heavily
loaded with mineral salts, including lesser quantities of fluorides.
Such water is unsuitable for the major beneficial uses, but in many
cases it constitutes the only available supply, with consequent
deleterious effects upon consumers. There is therefore an urgent
need for a reliable and economic method of demineralisation.

The primary need obviously is for those usages which are
already existent viz. human consumption and watering of stock. The
quality requirements of water for the latter purpose is, however,

/not.....

not so critical, as was pointed out above. The problem may thus be condensed to that of supplying demineralised water for human consumption only. Since arid regions are of necessity extremely thinly populated, it is essential that any proposed process should cater for the treatment of small quantities of domestic water, such as may be used by individual dwellings and expecially farmhouses.

In cases where water of suitable salinity but excessive fluoride concentration is available it will obviously be advantageous to remove the fluoride ions selectively. Such water is at present being used by a large number of individual farmers, by some isolated communities and by a few smaller towns. A defluoridation process should therefore provide for treatment of both small and large quantities of water.

It is thus concluded that the basic requirements are :
A. a process for demineralisation of excessively saline water in small quantities, say 2 to 5 gallons per day, and B. a process for defluoridation of fluoride bearing water of suitable total salinity - the process being adaptable for treatment of, from 5 to 5000 gallons of water per day.

These two aspects of saline water purification are reported separately in the ensuing chapters.

TABLE II

THE COST OF DEMINERALISATION

Desalting Method	Cost per 1000 galls. (from Sea Water)	
	Claimed	As used in S.A.
Ion Exchange	Not suitable above 2000 p.p.m. T.D.S. Estimated cost £7:0:0.	-
Evaporation	12/- (Triple-effect)	£1:0:0 (6-effect at Luderitz)
Compression Still	9/6 Power = 100 K.W.H./1000 galls.	£1:10:0
Freezing	No costs available	
Solar Distillation	10/6	£3:6:0

Electrical Methods	Power Consumption in K.W.H.	Total Cost
Electrolysis (30)	180	15/- (For partial (treatment (only.
" (36)	540	£1:10:0
Electrodialysis (38)	20	4/2
" (36)	40	4/4

A.   CHEMICAL PROCESSES.

A,1.   Ion-exchange first became an accepted method of demineralisation as a result of the work of Adams and Holmes (29). The process is based on the reversible ion-exchange properties of certain organic resins.   Thus acidic groups, particularly sulphonic groups attached to solid organic media will exchange cations in water, while synthetic resinous materials containing basic groups especially amines and quaternary ammonium groups will reversibly exchange anions.   When saturated, the exchange media are regenerated with dilute solutions of sulphuric acid and sodium hydroxide solutions respectively, followed by thorough rinsing.
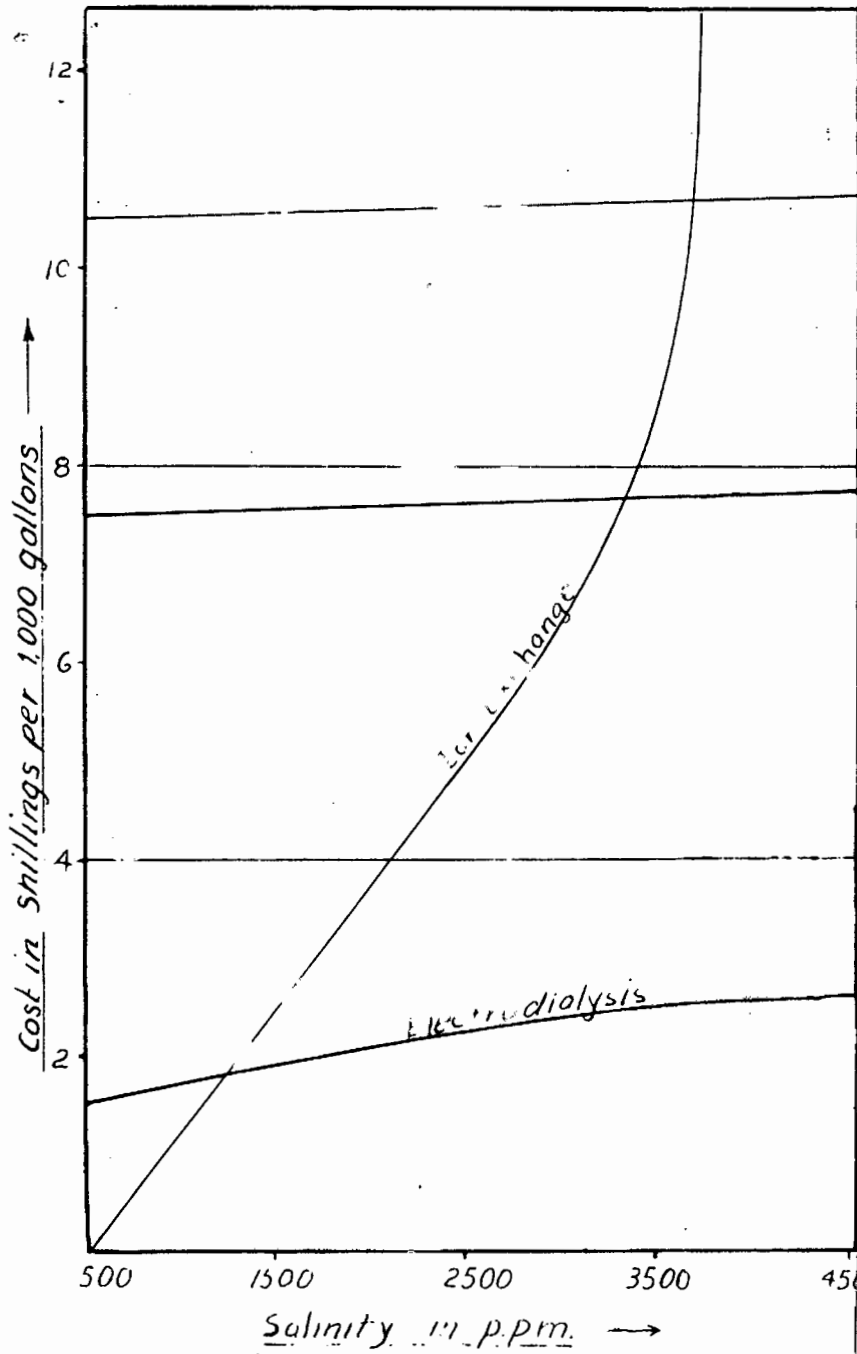
Figure 2   VARIATION OF COST

The more recent development of mixed bed ion-exchangers has made possible the complete demineralisation of water.

The cost of demineralised water produced by ion exchange is directly proportional to the quantity of salt to be removed from the raw water i.e. its salinity. For high salinities e.g. sea water, the process becomes completely uneconomical since 20 to 30 times the amount of water produced is then required, just to wash the regenerating solutions from the bed.(30). Recent work in Palestine (31) indicates that the economic limit of ion exchange demineralisation is reached when the raw water contains 2,000 to 2,500 p.p.m. total salines which is less than one-tenth the saline concentration of sea water.

A.2. Precipitation of dissolved salts with silver salts followed by lime treatment has been described and patented (32, 33) but the cost of such treatment is quite prohibitive (30). Conventional lime-soda softening of water involves precipitation of the calcium and magnesium ions and it constitutes the only economic method of partial demineralisation by precipitation.

A.3. Modern Developments.

More recently work sponsored by the Saline Water Conversion Programme of the United States Department of the Interior, has focussed attention on Solvent Extraction (34) and the use of osmotic membranes.(35).

Desalting of saline water by means of solvent extraction is being investigated at the Agricultural and Mechanical College of Texas under direction of Dr. D.W. Hood. The principle steps in the process are as follows :- The saline water is mixed with an organic solvent with which it is only partially miscible. The resulting ternary mixture then forms two liquid phases, the first a concentrated brine, containing

/little .....

little solvent and the second a mixture of water and solvent containing little salt.   The former is rejected while the latter is separated and its temperature changed in such a way that two phases are again formed.   The solvent phase is then recycled and the water phase is purified so as to remove the small amount of solvent which it contains.

Particular success has been obtained with the use of 2-ethylhexylamine.   Calculations indicated that the salt concentration of saline water could be reduced by 89% in a single cycle. Although the yield of water is as yet small, the technical feasibility of the process has been demonstrated.   It remains to be seen, however, whether it will be economically feasible.   In any case it is doubtful whether the process will be applicable to small installations since the complicated plant and operational procedure would render it unattractive to individual users.

Desalting with osmotic membranes is being studied at the Universities of California, New York and Florida by Drs. G.L. Hassler, G.W. Murphy and C.E. Reid respectively.   The process utilises "reverse-osmosis" i.e. artificial pressure in excess of osmotic pressure on the solute side of a semipermeable membrane. The use of fluid osmotic films, perm-selective membranes and a number of plastic membranes are being studied respectively by the above workers.

In its present state of development the use of cellulose acetate membranes has been found most efficient.   Saline water is forced through the membrane under c.a. 700 p.s.i. pressure, upwards of 90% of the salt being removed thereby, but the rates of water transfer are very low viz. 1 ml./sq.cm/day.   The membranes broke down after 36 days of continuous operation.

This work remains for the present rather speculative and in any case much time will be spent before practical application can be contemplated.

B.   ELECTRICAL PROCESSES. .   .

B, 1.   Electrolysis.   In the well-known process of
electrolysis, cations migrate towards the cathode while anions
move towards the anode.   If therefore, a porous diaphragm be
interposed between the two electrodes some separation of ions can
be effected.   The process is of course far from complete on
account of diffusion taking place in the reverse direction.
Briggs (30) developed such an apparatus which has found some
application in the treatment of boiler water.   In this application,
only the catholyte stream, which becomes alkaline due to formation
of sodium hydroxide at the cathode, is used.   The process is
therefore rather wasteful and for high concentrations of salt such
as exist in sea water it is impracticable.

A more efficient application of electrolysis utilises
reversible silver - silver chloride electrodes separated by a
porous diaphragm (36).   In this case the anolyte is demineralised,
the chlorides being fixed on the electrode while cations migrate
through the diaphragm into the cathode compartment.   When the
anode is saturated with silver chloride the polarity of the
electrodes is reversed.   The process involves several practical
difficulties such as insufficient adherence of silver chloride to
the anode and it is obviously only applicable to the removal of
halides.

B, 2.   Electrodialysis with membranes which are selective in
the ions which they will pass, constitutes the most recent
development in the field of water demineralisation.   The success
of this process depends on the use of membranes with ion-exchange
properties (37).   If such cationic and anionic membranes are
arranged alternately and an electric field be imposed across them,
ions will migrate selectively and consequently water in alternate

/compartments .....

compartments will respectively be mineralised and demineralised.
The flow through the respective membrane compartments is then
arranged so that the concentrated brine constitutes about one
fourth of the input water.   Using a battery consisting of some
200 membranes it has been possible to effect demineralisation of
sea water at a current consumption of 20 to 40 K.W.H. per 1000
gallons of fresh water produced (36 & 38).   These figures
compare favourably with the energy consumption of the most
advanced demineralisation units at present in use (vapour-
recompression stills require 80 to 100 K.W.H. per 1000 gallons).
It is thus claimed that the cost of electrodialytic demineralisation
will be less than half that of the most economic evaporation of
sea water.

The cost of electrodialysis, as in the case of ion
exchange, varies with the concentration of salts in the raw water
(See figure 2). Demineralisation of water with salinites less
than that of sea water should therefore be even more economical.
Natural waters, however, generally contain appreciable quantities
of calcium and magnesium salts, which precipitate in those
compartments where the ions are concentrated, with consequent
injury to the semi-permeable membranes.   This ill-effect was
only discovered very recently by the National Chemical Research
Laboratory.   It is thus necessary to soften natural water by
conventional soda-lime treatment prior to electrolysis and
consequently the total cost is again increased.

The main disadvantage of the process of electrodialysis
is that it requires a regular, large supply of electric current
as well as skilled supervision and regular replacement of membranes.
As such its application to isolated South African communities and
individual households would seem remote.

/Thermal Methods.

C. THERMAL METHODS.

In contrast to chemical and electrical methods where salt is removed from solution, thermal methods remove water molecules from the saline solution. The cost of producing fresh water by these latter methods is therefore independent of the salinity of the raw water, but higher salt concentrations will influence maintenance costs slightly, in that, for example additional scale formation will necessitate more frequent cleaning.

C,1. Thermal Evaporation is the only method of demineralisation that has, as yet, found limited practical application. During the last 20 years conventional multiple effect evaporators have been superceded by vapour-recompression stills, for which remarkably high efficiencies are claimed (30). The latter type has the additional advantage of compact design and automatic operation.

In South Africa, conventional evaporators have been more successful (1), mainly on account of the high cost of diesel fuel, and of maintenance, required by vapour-recompression stills. Alternative forms of motive power may be used, but diesel driven compressors are obviously the only possibility in isolated locations.

Distillation at pressures above the critical value for water, has been suggested by von Platen (39) who showed thermodynamically that far less energy is required for distillation at, or above the critical pressure. There are, however, practical difficulties involved in the construction and operation of such equipment and it remains to be seen whether any real economy will result.

On the whole it seems unlikely that any substantial

/improvement .....

improvement can be effected on the present efficiency of commercial distillation plants. It has been calculated that the minimum "concentration" energy to divide sea water into brine and fresh water, approximates to the free energy difference between sea water and fresh water i.e. 3 K.W.H. per 1000 gallons of fresh water (40). This estimate of absolute minimum energy required, makes no allowance for friction, heat or other losses which would necessarily occur in any actual process that could be devised.

The best efficiency obtained with distillation plant thus far, has been c.a. 100 K.W.H. per 1000 gallons which is very much higher than the above theoretical minimum. Some other processes, however, are even more wasteful of energy while those with lower energy consumption remain impracticable. It is obvious therefore that mechanical distillation can only be resorted to when a cheap source of fuel is available or when sheer need of fresh water necessitates its use.

C,2. <u>Freezing</u> provides partial separation of fresh water as ice crystals and may therefore be utilised for the production of fresh water. The latent heat of freezing is of course much less than that of distillation but the cost of refrigeration is again very much higher than that of heating. In addition the practical difficulties involved in ensuring fine ice crystal formation and subsequent removal of these crystals, have thus far prevented any success with the process.

C,3. <u>Utilisation of Solar and other Natural Sources of Energy</u> such as winds, tides and thermal differences in the ocean, are often mentioned in literature (30, 41, 42, 43) as means for reducing the cost of demineralisation, but up to the present, only solar distillation has been proved to have practical

possibilities. The latter process is dealt with more fully, in part II of this chapter.

II. $\underline{S O L A R \quad D I S T I L L A T I O N}.$

The various methods of demineralisation reviewed in part I of this chapter, may each find specific applications e.g. ion-exchange is useful when water of relatively low salinity is available, electrodialysis again, will be practicable when the necessary services are available while thermal evaporation represents a conventional and reliable method of producing pure water from highly saline sources. The latter process would obviously have solved the demineralisation problem, were it not for its costly consumption of fuel - a primary natural resource. . The heat energy required for distillation of water, can of course be provided by the sun's radiation and is in fact used extensively in the well-known natural process of rain-making. It is therefore, not surprising that artificial solar distillation has fascinated man's interest for the past century.

Artificial solar distillation was first employed commercially in 1872, by a Chile mining company which continued its operation for 35 years. A descriptive record (44) of this installation indicates that it consisted of shallow wooden troughs which were covered by inclined glass panes. The highest water yield was approximately one pound per square foot of pan area per day, but no record of solar radiation was taken so that correlation of distillate yield with radiation received by the still is impossible.

Solar distillation was thereafter spasmodically studied and found unsuccessful on account of low heat efficiency and high capital cost. During World War II, the need for supplying fresh water to life rafts stimulated intensive study on collapsable,

/floating......

floating type, solar stills but no information regarding this work was available at the time of the present investigations.

A preliminary unpublished report on solar distillation experiments conducted in the Virgin Islands was prepared by the British Commonwealth Scientific and Industrial Research Office in 1951. This report indicated that about 1.5 lbs. of distillate were obtainable per sq.ft. per day. This yield would probably correspond to an efficiency of about 70% utilisation of incident solar radiation, but no definite results were recorded. The practical application of solar distillation thus remained speculative on account of uncertainties regarding cost, reliability, technical workability and performance under various climatic conditions.

Theoretical considerations indicated that the capital cost of a solar still would be comparatively high due to the following inherent characteristics of solar energy :

   (1) its intermittency and variability resulting in
       only 25% utilisation of the continuous capacity
       of equipment; and

   (2) its relatively low concentration (550 calories
       per cm.^{2} per day, at best as compared with
       300,000 to 800,000 for steam boilers) requiring
       large heat exchange surfaces.

It was thus estimated that water produced by artificial solar distillation would be dearer instead of cheaper than that produced by conventional distillation.

Notwithstanding these disadvantages it was considered that solar distillation held promise of successful application in South Africa. The following factors prompted this decision :

   (1) No alternative demineralisation process can be operated trouble-free and without skilled supervision.

   (2) Local requirements are primarily for small, self-contained, household units, for which initial cost of construction should be moderate. Although the actual cost per 1000 gallons of distilled water produced might be comparatively high, it must be

remembered that thousands of gallons are <u>not</u> required by individual households.

(3)   In arid regions where fresh water is scarcest, there is also an abundance of sunshine since humid atmospheres, the chief absorbant of solar radiation, must of necessity be at a minimum.   In South Africa especially, the long and plentiful hours of sunshine favours utilisation of solar distillation.   With such free energy, running costs could be kept at a minimum.

(4)   The absence of reliable data on the performance of solar stills indicated the need for a programme of research. In addition all previous solar stills had been operated in countries with different climates to that of South Africa and since local climatic and environmental conditions would have a profound effect upon the use of solar stills, it was considered that local experimentation was urgently required.

The present investigations were thus undertaken to supplement the deficiency of quantitative and comparative data on solar distillation techniques, particularly with regard to cost and efficiency.   The primary objectives were :

(1)   Quantitative correlation of distillate yield with local climatic conditions, especially radiation.

(2)   Development of means for improving the performance of solar stills.

(3)   Development of cheap and efficient solar stills which can if necessary be home-made.

(4)   Assessment of the practical feasibility of such stills when
used under South African conditions by individual households.

A.   THE APPARATUS.

In deciding upon the apparatus to be used for the investi-
gations, several alternatives suggested themselves.   The basic
requirements of a solar distillation unit are : (a) a solar heat
collector in which saline water is heated, (b) an evaporator and (c)
a condenser.   These requirements can be met by a variety of designs,
for example the heat collector may be a focussing or flat plate type
while the evaporator and condenser may follow the design of any of
the many types commonly used.

The choice of apparatus was, however, strictly limited by
the objectives of the investigation, viz. to develop the simplest
and cheapest device compatable with reasonable efficiency and trouble-
free operation.   It was thus decided not to use focussing heat
collectors since these must be rotated with the sun in order to
"strike" the heat absorber continuously.   The intricate mechanism
required for such rotation would defeat the above object.   It was
further decided that combination of the three basic components into
one unit would be most desirable.   Such a combination can be achieved
in the apparatus which is shown schematically in figure 3.   This
apparatus consists of a shallow black pan which contains the saline
water to be evaporated.   This pan is covered by inclined transparent
(glass) panes which fit snugly on the pan.   The panes are inclined
at an angle of 45° so that condensate which collects on the inside of
the hood, runs down the panes into collecting troughs.   Solar stills
of similar general design were also used in Chile (44) and the Virgin
Islands and this added to its attraction in view of possible
comparison of results.

It was therefore decided that a conventional inclined plate
solar still would best suit the purpose of the investigations.   This

/decision .....

GLASS PANES

CONDENSATE
DEFLECTORS

CONDENSATE
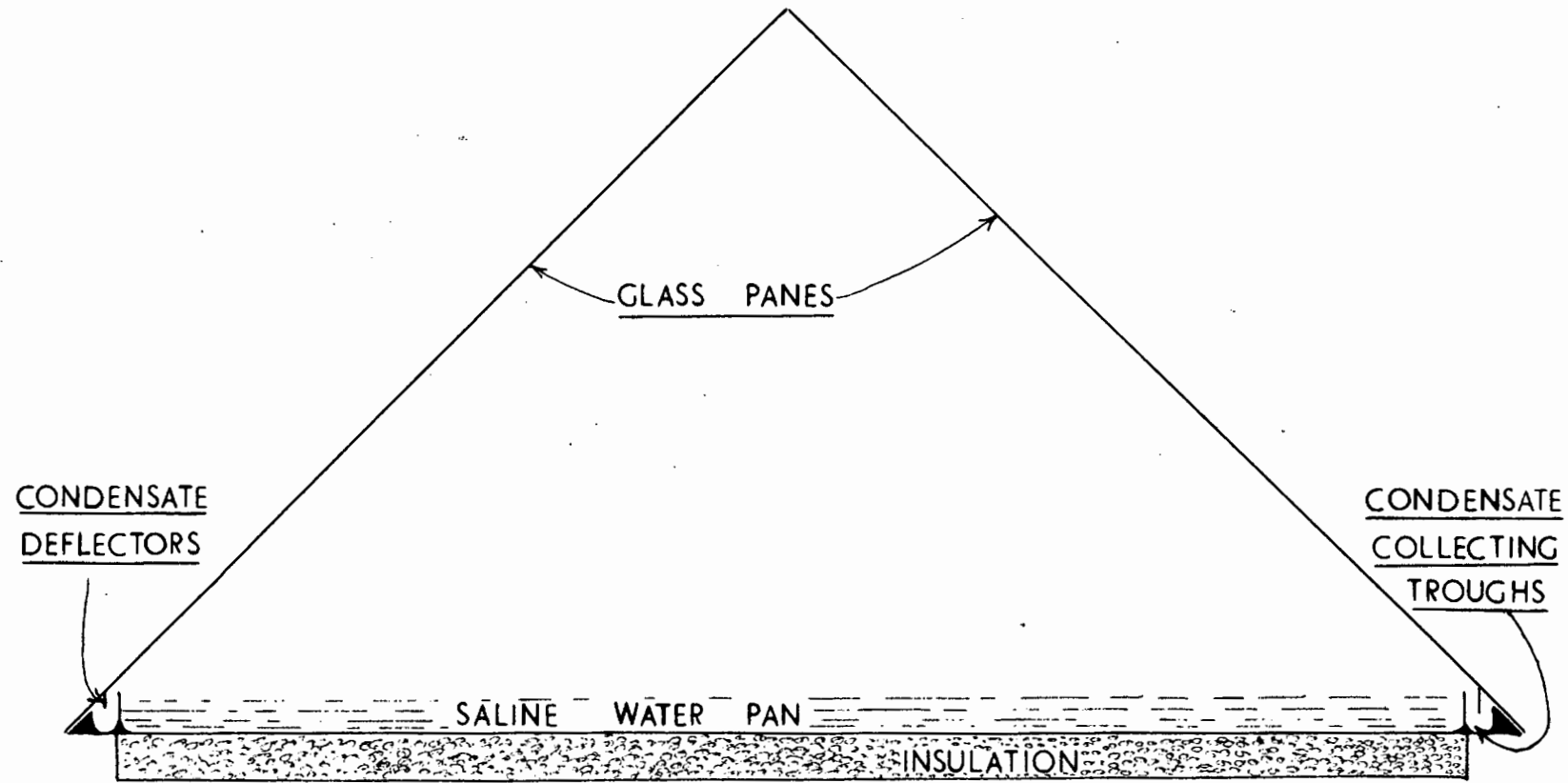COLLECTING
TROUGHS

SALINE WATER PAN

INSULATION

Figure 3   SCHEMATIC SECTION OF SOLAR STILL

decision was subsequently (1954) affirmed by a report from Dr. G.O.G. Löf (45) who reviewed the economics of solar distillation under contract for the United States Department of the Interior. In arriving at the actual design used, the principles underlying the operation of inclined plate solar stills were first given careful consideration.

A.1. Principles underlying its Operation.

A solar still of the general design described above operates because the glass cover is transparent to visible radiation but opaque to long-wave heat radiation. Thus, solar energy passes readily through the glass to be absorbed by the black coating of the pan as heat energy. This heat energy then cannot escape and consequently heats the pan with its contents. At the same time the glass surface, by virtue of its contact with the atmosphere, remains relatively cool. Water vapour will thus diffuse from the pan to condense against the glass surface whence it is collected as indicated.

For maximum efficiency of this process the following factors are obviously of prime importance :

(a) The pan must be maintained at as high a temperature as possible. This in turn implies that the pan must be well insulated, while maximum radiation should impinge upon it, i.e. the pan cover must be as transparent as possible. In addition the pan should have good light absorbent properties.

(b) A substantial temperature differential should be maintained between the evaporating liquid and the condensing surface. The cover should therefore have a high diathermancy i.e. absorb a minimum of radiation so as to remain as cool as possible.

(c) Since the rate of diffusion of water molecules inside the still is slow, the condensing surface should be close to the pan. A flat cover should thus be advantageous but the adherence of water droplets to glass is limited by the surface tension and a sloping surface is therefore essential.

(d)   Several practical requirements such as orientation and
positioning of the still, weatherproof construction and
collection of distillate without loss, must be complied with.

A2.   Design of the Experimental Still.

From the foregoing considerations it is clear that the
construction of a solar still must satisfy a number of requirements.
The necessity of providing a cheap and simple apparatus, however,
limits the design to provision of only the essential components.

The apparatus depicted in figures 4 and 5 was thus con-
structed in the workshops of the Council for Scientific and Industrial
Research.   As will be seen from figures 4 and 5 the apparatus con-
sisted essentially of a shallow evaporating pan on which was supported
a removable glass turret.

The evaporating pan was contained in a shallow wooden box
which was first filled with a 6" layer of vermiculite.   The box was

/supported .....

Figure 4

Experimental Solar Still with mirrors in position.
Photographed at 8 a.m.

North Elevation of Experimental Solar Still Photographed
at 3 p.m. (Note rapid condensation at this time of the
day)

Figure 5

North Elevation of Experimental Solar Still Photographed
at 3 p.m. (Note rapid condensation at this time of the
day)

supported 9" off the ground so as to allow for reception of distil-
late and for inspection of insulation.   The pan was made 4' x 4' x
3" deep and a channel 2" wide x 1½" deep was provided round its
perimeter.   A delivery pipe from the channel passed through the
wooden base into a receiver.   The pan was painted pitch black and
the channel flat white.

The hood consisted of a wooden frame mounting glass panes
of 3/16" thick.   It was attempted to position the glass as close
as possible to the pan and to provide a maximum transparent surface.
The wooden construction, however, necessitated a height of 2'5"
from the pan to the apex while the clear area of each of the four
panes was 23" x 33".   At the lower edge of the glass panes,
immediately above the condensate channel, deflectors were provided
in order to direct condensate from the glass surface into the channel.
These deflectors consisted of "perspex" strips, cemented on to the
glass with a waterproof adhesive.   The turret was made to fit
snugly on to the base so as to comprise a sealed unit.

The unit was located on the grounds of the University of
the Witwatersrand (latitude 26° 11' S, longitude 28° 02' E, altitude
5700').   It was placed on a level concrete slab with the ridge
pointing due east and west.   Sufficient clear space was available
around the site to allow for solar radiation of the still from
6 a.m. to 6 p.m.

A,3.   Operation of the Still.

The still was put into operation in May, 1952 using
artificial sea water as the medium evaporated.   The pan was filled
to a depth of 1.2 inches using 10 Imp. gallons of water which
contained 2.65 lbs. NaCl, 0.24 lbs. MgCl$_2$, 0.33 lbs. MgSO$_4$, 0.11
lbs CaCl$_2$ and 0.07 lbs. KCl.   The consistency of the solution
was kept constant by returning collected distillate to the pan
daily, while any losses due to leakages of vapour and/or con-
densate, were made up with distilled water.   The depth of liquid

/in .....

in the pan was kept constant throughout the run of the present
experiment.   Careful record of the daily distillate yield was kept
and the temperature of water in the pan was recorded at 2 hourly
intervals during the day time.   The inner surface of the glass
panes were well cleaned before operation was commenced and con-
sequently film-condensation was obtained throughout the run of the
experiments.   It should be noted, however, that dirty condensing
surfaces will cause "drop type" condensation which may drop back
into the pan and scatter radiation unduly.   On windy days, dust
and dirt collected on the outer glass surfaces and affected the
transparency.   It was found necessary to clean the glass at least
every day.

In order to correlate distillate yields with prevailing
weather conditions, the following meteorological instruments were
installed at the still :

(1)   A bimetallic radiation recorder giving the total radiant
      energy in calories per sq.cm. incident on a horizontal
      surface.
(2)   A max./min. thermometer.
(3)   A "Steglitz" barometer.
(4)   A hygrometer.
(5)   Winds were recorded by visual observation.

The radiation recorder was first calibrated by the Weather
Bureau of the South African Department of Transport, and thereafter
check-calibrated at regular intervals by comparison with a portable
sub-standard radiometer.   Only total daily radiation values were
obtainable.   Other instruments were read at two-hourly intervals
during the day.

Operation of the still was thus continued until 15th July,
1954 when a vertical mirror was installed on the south side of the
still to reflect additional solar energy into the evaporating pan.
The mirror consisted of three stainless steel plates each 24" x 16"
providing a combined reflecting surface of 4' x 2'.

After three months operation with the mirror in position,
an additional aid to evaporation was introduced in the form of
cooling of the south facing glass panes.   For this purpose, water
was continuously sprayed on to the glass at the ridge and allowed to
run down into a trough whence it was recirculated.

A,4.   Difficulties experienced.

During initial operation of the still, the yield of
distillate was unduly low due to some structural defects which were
subsequently rectified as described below :

(a)   Soon after commencing the experiments it became apparent
      that the condensate deflectors were unsuitable.   They
      became severed from the glass in places, due to differential
      expansion upon heating.   The thin film of condensate there-
      after passed through the openings onto the wooden frame and
      was lost.   It was attempted to rectify this defect by
      replacing the "perspex" with glass strips, but leakages of
      condensate again occurred.   It was then found necessary to
      use metal deflectors which were bent round the lower edge
      of the glass so as to form a water seal.   (Figure 6).

      This experience indicated that provision of efficient
      condensate collectors was most essential.

(b)   The humid atmosphere of the still as well as the leakage
      of condensate caused the wooden frame to warp, with the
      result that the cover no longer fitted the pan base neatly.
      The partial clearance allowed air currents to pass in and
      out of the glass enclosure,. carrying with it water vapour
      which was thus lost..   In order to obtain a draught-proof
      seal, sponge rubber strips were inserted between the base
      and cover.   This proved effective but in practice a further
      improvement may be obtained by using a metal frame instead
      of wood.

(c)   A final difficulty experienced in operating the still, was
      the failure of the bitumin paint used for blackening of the
      evaporation pan.   The salt water together with wide temper-
      ature variations, of course subjected the paint to severe
      strain, but a plastic paint, used with a suitable primer,
      proved effective and retained its jet-black colour through-
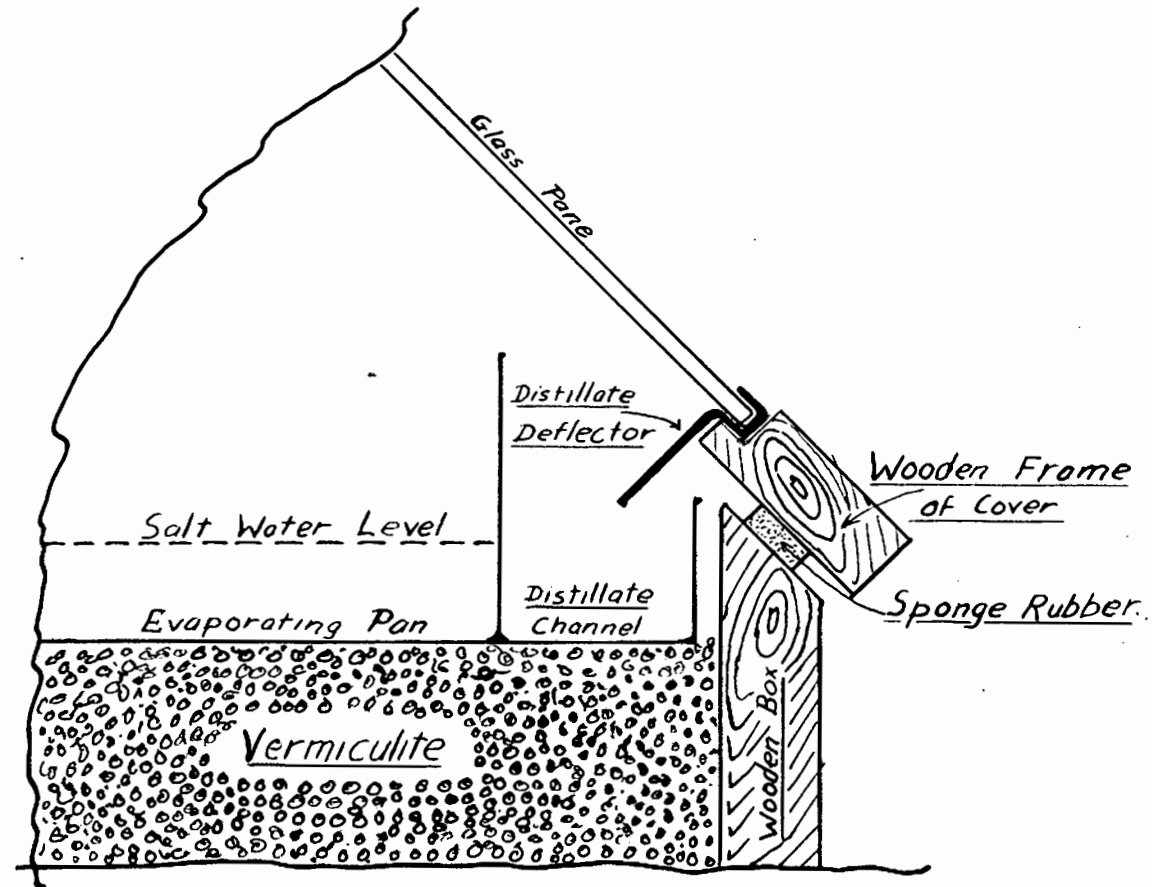   out the experiments.

Figure 6 SECTION OF STILL

Showing Fitting of Deflector

B. EXPERIMENTAL RESULTS

During the first year's operation the data obtained were unreliable on account of the difficulties experienced, but the results nevertheless gave a qualitative indication of what may be expected under local climatic conditions. The data recorded below refer to the 2nd year of operation from 1/6/53 to 15/7/54.

B.1. Effect of Radiation

It was at first attempted to correlate daily distillate yields with total daily radiation (see table III) by calculating the distillate yield per kilocalorie radiation received by the pan. This ratio was calculated as follows: The total daily radiation figure as recorded by the solarimeter was multiplied by a factor of 14.863 to give the total radiation received by the 16. sq. ft. of pan area in kilocalories (kcal). The distillate yield was then divided by the latter product.

TABLE III

DAILY VARIATIONS OF DAILY DISTILLATE YIELD WITH RADIATION

Date	Radiation cal./sq.cm.	Distillate yield ml.	Ratio ml./kcal.	Weather Conditions
1/9/53	522	3780	0.486	Fine and windy
2/9/53	453	3470	0.515	Fine but hazy
3/9/53	483	3750	0.522	Fine - no wind
4/9/53	502	3750	0.502	Fine- slight wind
5/9/53	488	3350	0.461	Fine but windy
8/9/53	498	3880	0.524	Intermittent clouds
9/9/53	532	3880	0.491	Fine -slight wind
10/9/53	523	4330	0.557	Fine - no wind
11/9/53	523	4130	0.531	Fine - no wind
14/9/53	598	4380	0.493	Fine - but windy
15/9/53	428	2500	0.393	Cloudy-strong wind
16/9/53	588	4190	0.489	Cloudy and windy
17/9/53	601	4640	0.520	Fine but windy
18/9/53	590	4750	0.542	Fine - slight wind
19/9/53	570	4640	0.548	Fine - slight wind
20/9/53	620	5120	0.555	Fine - slight wind
21/9/53	554	4780	0.581	Fine - no wind
22/9/53	543	4070	0.504	Fine - slight wind
23/9/53	523	4330	0.557	Cloudy - no wind
24/9/53	574	4620	0.542	Fine - no wind

A reasonably constant ratio was obtained for clear days, but rapid fluctuations of radiation values on cloudy days, caused irregularities which were probably due to the characteristics of the solarimeter used. The occurrence of winds also seemed to cause a decline in yield of distillate. (Note the lowered ratio for the 5th, 14th, 16th and especially the 15th September 1953).

Much better agreement was obtainable when weekly averages of radiation and distillate were compared. Such values are recorded in table IV.

These weekly ratios have been plotted against dates in figure 7b while figure 7a shows the variation of ratio with increased radiation.

TABLE IV

WEEKLY AVERAGE RATIO OF DISTILLATION TO RADIATION.

Date of week ending	Average daily Radiation cal/cm^2	Ratio of distillate to Radiation ml./kcal.	Date of week ending	Ave daily tio cal
21/6/53	298	0.474	10/1/54	
28/6/53	341	0.464	17/1/54	
5/7/53	319	0.483	24/1/54	
10/7/53	374	0.499	31/1/54	
19/7/53	344	0.509	7/2/54	
26/7/53	398	0.480	14/2/54	
2/8/53	395	0.481	21/2/54	
9/8/53	390	0.492	28/2/54	
16/8/53	396	0.502	7/3/54	
23/8/53	402	0.503	14/3/54	
30/8/53	446	0.508	21/3/54	
7/9/53	503	0.507	28/3/54	
13/9/53	539	0.526	4/4/54	
20/9/53	567	0.510	11/4/54	
27/9/53	565	0.546	19/4/54	
4/10/53	592	0.549	25/4/54	
11/10/53	578	0.542	2/5/54	3
15/10/53	583	0.547	9/5/54	3
25/10/53	546	0.543	16/5/54	3
1/11/53	696	0.570	23/5/54	3
8/11/53	508	0.547	31/5/54	3
15/11/53	458	0.512	6/6/54	3
22/11/53	611	0.542	13/6/54	3
29/11/53	536	0.520	20/6/54	2
6/12/53	559	0.515	27/6/54	3
13/12/53	669	0.543	4/7/54	3
20/12/53	507	0.514	12/7/54	38
27/12/53	669	0.541	14/7/54	34
3/1/54	571	0.526		

Overall average of daily radiation = 460 cal.
Average ratio of distillate to Radiation = 0.50
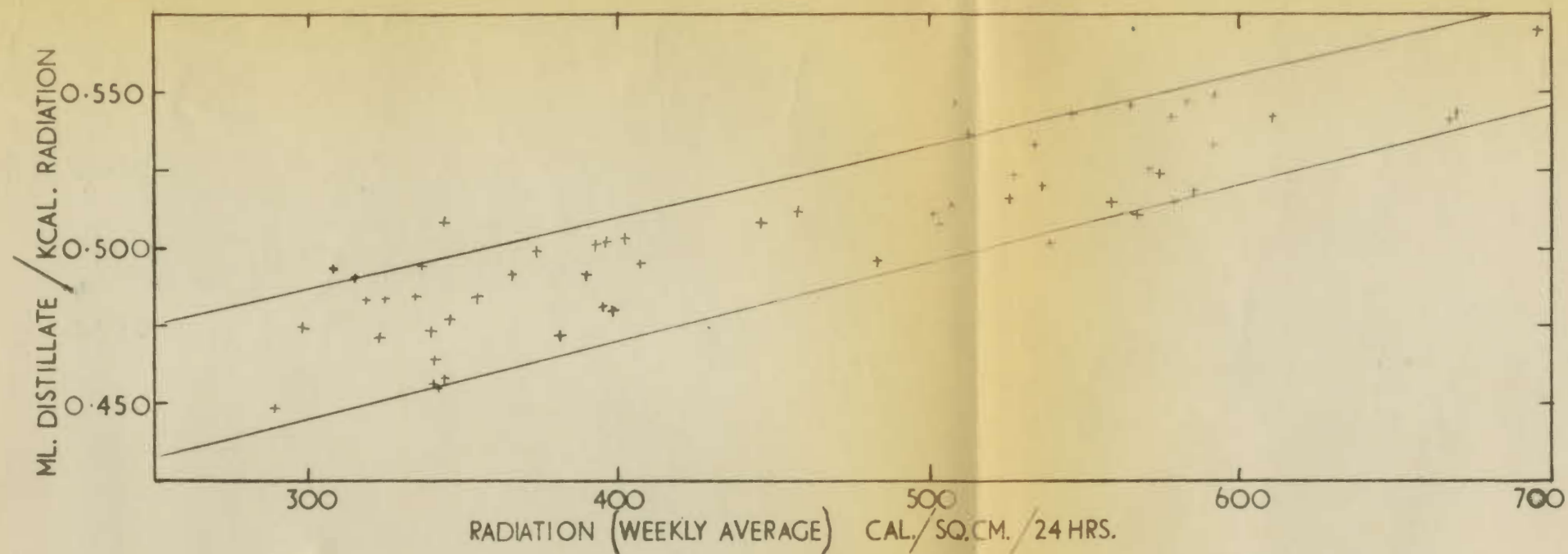Average daily yield of distillate = 3460 ml. c

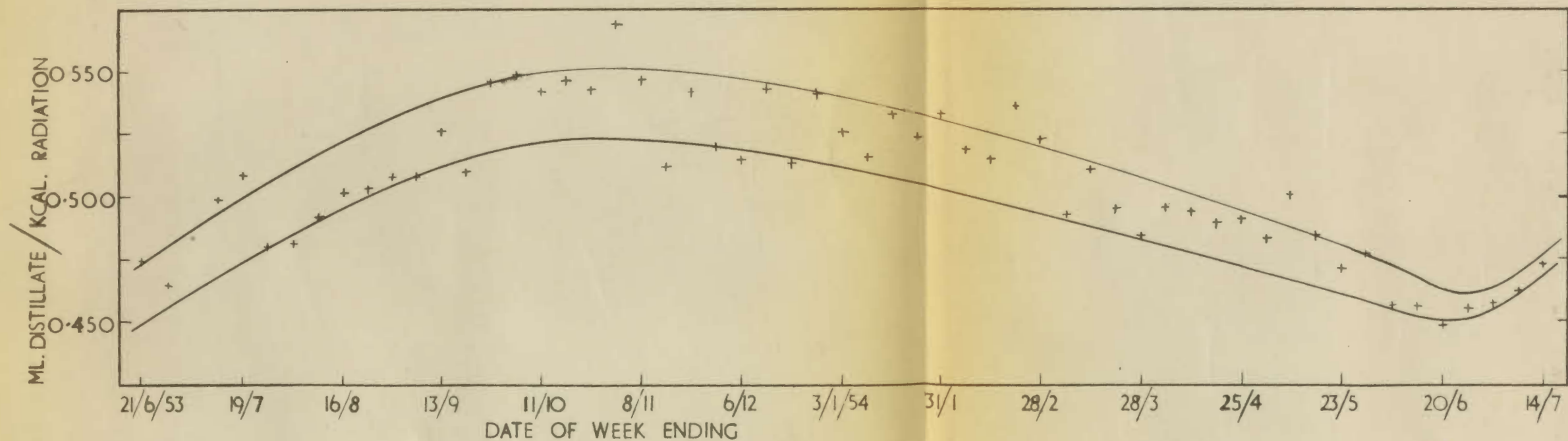Figure 7a. VARIATION OF DISTILLATE RATIO WITH RADIATION

Figure 7b. SEASONAL VARIATION OF DISTILLATE RATIO

Observations

(i)   From the data of Table IV the average yield of distillate
        was calculated to be 0.505 ml. per kcal. of radiation
        received by the pan. Theoretically the heat required to
        distill 0.505 ml. of water would be: 0.505 x 20 cals.
        for heating the liquid in the pan through 35.5°F i.e.
        20°C to the average bath temperature: (refer 2,a, (vi)
        and 2b of this section) plus 0.505 x 574 cals. for
        supplying the latent heat of vapourisation at a
        temperature of 101.7°F. (refer 2, a, (vi) of this section).
        This amounts to a total of 300 cals. indicating an overall
        average heat efficiency of 30%.

(ii)   Average radiation during summer 22/9/53 to 21/3/54 was
        550 cals/cm^2/24 hrs. while during winter 21/6/53 to 20/9/53
        and 22/3/54 to 20/6/54 it was 383 cals/cm^2/24 hrs. During
        the period of observation the lowest radiation value (41
        cals./cm^2/24 hrs) was recorded on 19/10/53 while a
        maximum of 893 cals/cm^2/24 hrs. was recorded on 8/11/54.
        High radiation values, 800 cals./cm^2/24 hrs. were also
        recorded in October, December and January, but due to
        frequent rain and cloudiness severe fluctuation of
        radiation occurred and the average monthly radiation
        remained but slightly higher than the average for the
        whole summer.   During winter, daily radiation values were
        more constant.

        It is thus clear that clouds, fog and rain are predomina-
        ting factors in determining the amount of radiation im-
        pinging on a solar still at ground level.

(iii)   Based on weekly averages, the lowest yield of distillate
        was 2000 ml./day while the highest was 6000 ml/day.
        Reasonable yields of distillate may thus be expected even
        with cloudy or rainy weather.

                                                    (iv) .../

(iv)   From the data of table IV it was calculated that
the distillate yield per unit radiation received by
the pan was higher in summer than in winter viz.0.529 and
0.438 ml. per kcal. respectively.   This increased ratio
is also depicted in figure 7b which shows a fairly
regular variation of ratio with time of the year.

In figure 7b it will also be noted that fluctuations
of the ratio was more severe in summer when frequent rain,
thunderstorms and cloudy conditions occurred which
resulted in irregular daily radiation.   It may therefore
be concluded that higher efficiencies are obtainable with
the increased radiation experienced during summer and that
the irregular radiation, i.e. fluctuating from day to day,
caused severe fluctuations of efficiency.   Such a
conclusion is also supported by the graph of figure 7a,
which shows an increased distillate/radiation ratio at higher
radiation values.

This conclusion, however, neglects the effect of
increased atmospheric temperature which always
accompanies increased radiation and which may be primarily
responsible for the improved efficiency.   This effect
of atmospheric temperature is evaluated under 2d of this
section.

(v)   On the whole the results show that the variation of
distillate/radiation ratio is sufficiently regular, within
the range of the curves depicted in figures 7a and b,
to conclude that radiation intensity, directly or
indirectly via its accompanying climatic conditions, is
of major importance in determining the performance of a
solar still.

B,2.   Temperature

Next to radiation, temperature may be expected to
have an important effect upon distillation.   The following
items justify consideration.

a) Bath. .../

B,2,(a) <u>Bath</u>.   The construction of a solar still provides
specially for absorption of radiant energy.   It must
therefore be expected that the temperature of water in
the evaporating pan of the still will increase with
radiation.   The temperature variations for a clear day
in winter (8/7/53) have been plotted against time of day
in figure 8a and for a clear day in summer (18/1/54)
in figure 8b.   These graphs may be taken as typical
of the daily temperature variations although of course
the actual values altered.

<u>Observations</u>

(i)   Bath temperature was largely dependent upon
the amount of radiation impinging on the still. The
curves of figure 8 follow that of the recording
solarimeter (not shown) closely, except that it
lagged behind some 2 hours as indicated under (iv)
and (v) below.

(ii)   Low incidence radiation, i.e. in the early
morning and late afternoon, was almost wholly reflected
from the surface of the water in the pan with the
result that very little radiant energy was absorbed.
This was of special significance in the morning since
atmospheric temperature then rose more rapidly than
did the bath temperature, while distillation could
obviously only proceed when the bath temperature
exceeded atmospheric temperature.   On clear days the
bath temperature first exceeded ambient temperature,
about 2 hours after sunrise.   It thereafter rose
rapidly until a maximum value was attained at about
14.00 hours.

(iii)   At sunrise the temperature of the water in the
bath was always below atmospheric indicating that
during the night distillation had continued until the
heat absorbed thereby had reduced the temperature of
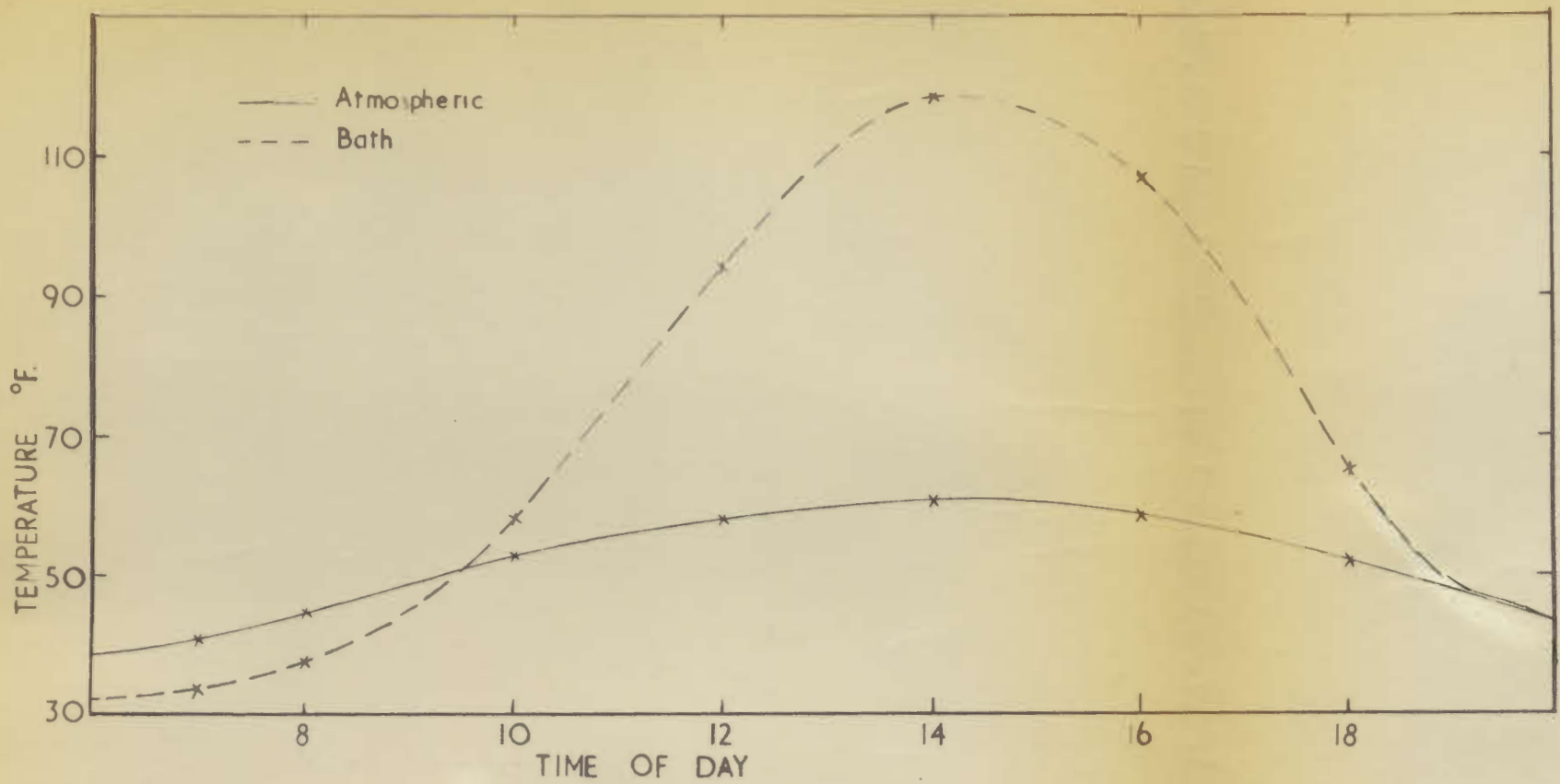the bath almost to minimum night temperature.
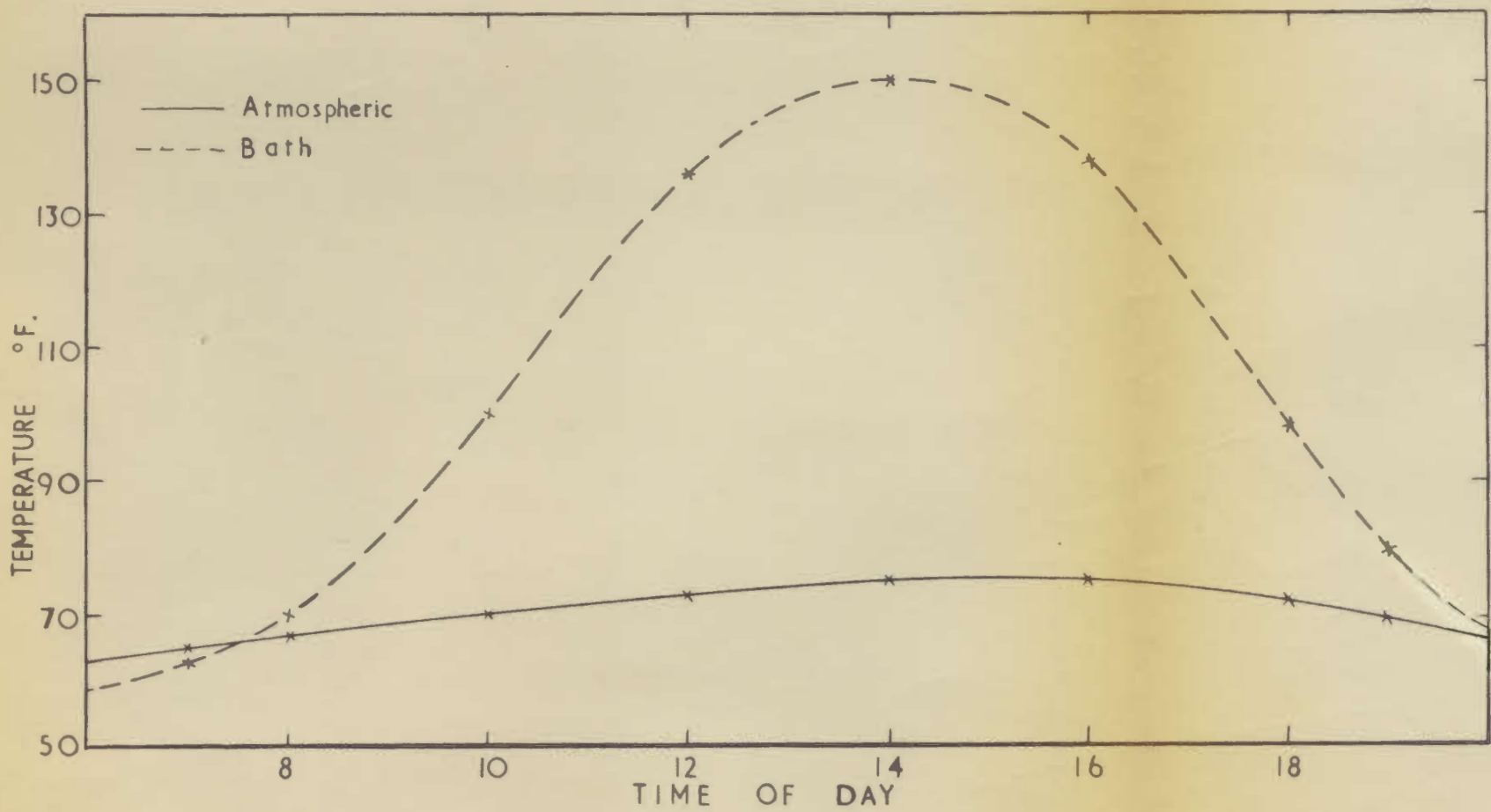
(iv) .../

Figure 8a   TEMP. CHANGES on 8/7/53

Figure 8b   TEMP. CHANGES on 19/1/54

(iv)   Peak bath temperature was always obtained from 1 to 2 hours
after maximum radiation (theoretically at noon).   This is due to
the fact that during the period of increasing radiation, absorbed
radiant heat is used both for heating the bath contents and for
evaporation. The bath temperature and with it the rate of
evaporation will consequently increase until the heat requirements
equal the heat input, but at maximum radiation this has not yet
occurred due to the heat ballast of the pan and its contents.

(v)   After 14.00 hrs., the bath temperature dropped rapidly with
simultaneous rapid distillation, caused by decreasing condenser
(air) temperature. Distillation thus continued long after sunset
by virtue of the heat stored in the bath contents.

(vi)   During summer, on clear days, the bath temperature remained
significantly higher than atmospheric temperature for an average
of 12 hours at an average temperature of 109.9°F. During winter
the average duration of elevated bath temperature was 10 hours and
the average temperature during these hours was 93.5°F. The
average bath temperature during the period when distillation
proceeded was thus 16.4°F higher in summer than in winter and for
the whole year the average temperature was 101.7°F.

B,2,
(b) Atmospheric. Typical ambient temperature variations have also been
plotted in figure 8.   It will be noted that atmospheric temperature
showed comparatively small variations during the hours of the day.
Distillation started when the bath temperature exceeded atmospheric
temperature and was thereafter apparently proportional to the
temperature difference.

The average day temperature during summer was 12.4°F more
than during winter viz. 72.4° and 60°F. respectively.   During
summer therefore, the still was operating at higher temperatures
than in winter and hence by virtue of increased vapour pressure it
must be expected that a higher rate of distillation was obtainable
in summer.   Evaluation of this effect is further discussed under
item d. of this sub-section.

B,2, (c) Differential

B,2,(c) Differential.   It may be expected that the rate and
volume of distillation will depend largely upon the
temperature gradient between bath and condenser.   In
order to assess whether any such relation did in fact
exist, daily volumes of distillate were plotted against
the integral of differential temperature with time, for
respective days. (Figure 9a).   The value of the daily
integral is expressed as $^\circ$F.-hours and represents the
product of the mean temperature difference between bath
and air multiplied by the hours during which such difference
remained positive.   Such values may be obtained by
measuring the areas between the temperature curves (as
was plotted for two days only in figure 8) for individual
days.   For the purpose of figure 9, however, it was
calculated by integration of observed temperature
differences with time.

In order to correlate temperature difference with
radiation, daily radiation values were plotted against the
above differential temperature - time, integral for the
respective days (Figure 9b).

Observations

(i)   The values plotted in figure 9a indicate a
regular relation between differential temperature
and distillation, within the range of the two curves.
It will be noted that the curves slope upward at an
increasing gradient indicating that higher distillation
yields per unit temperature differential were obtained
with increasing temperature differential values. This
conclusion is in agreement with observation (iv) of
"Effect of Radiation" subsection B,1, and with figure
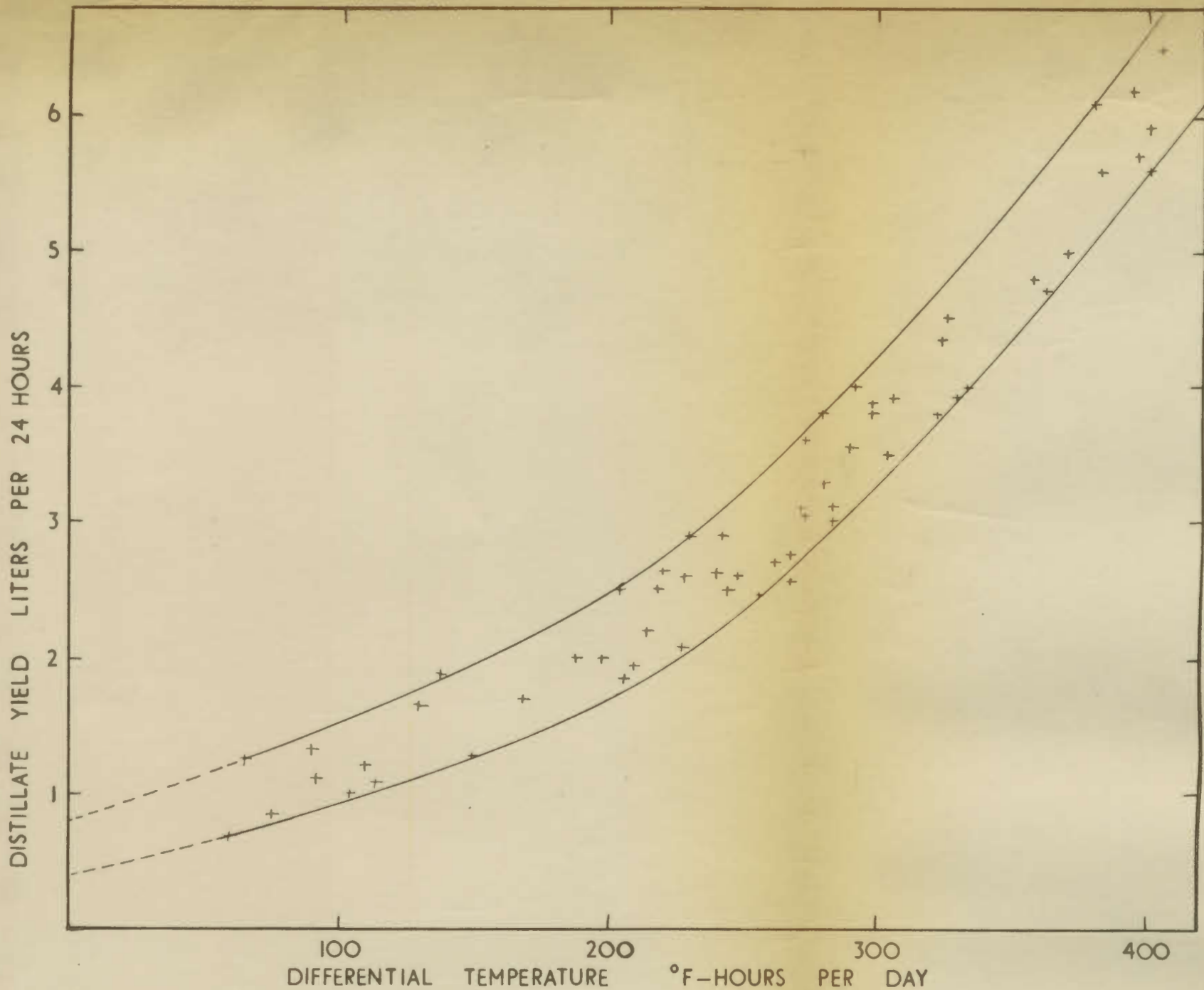7a viz. that a higher distillate yield per unit

radiation ../

Figure 9a   VARIATION OF DISTILLATE YIELD WITH
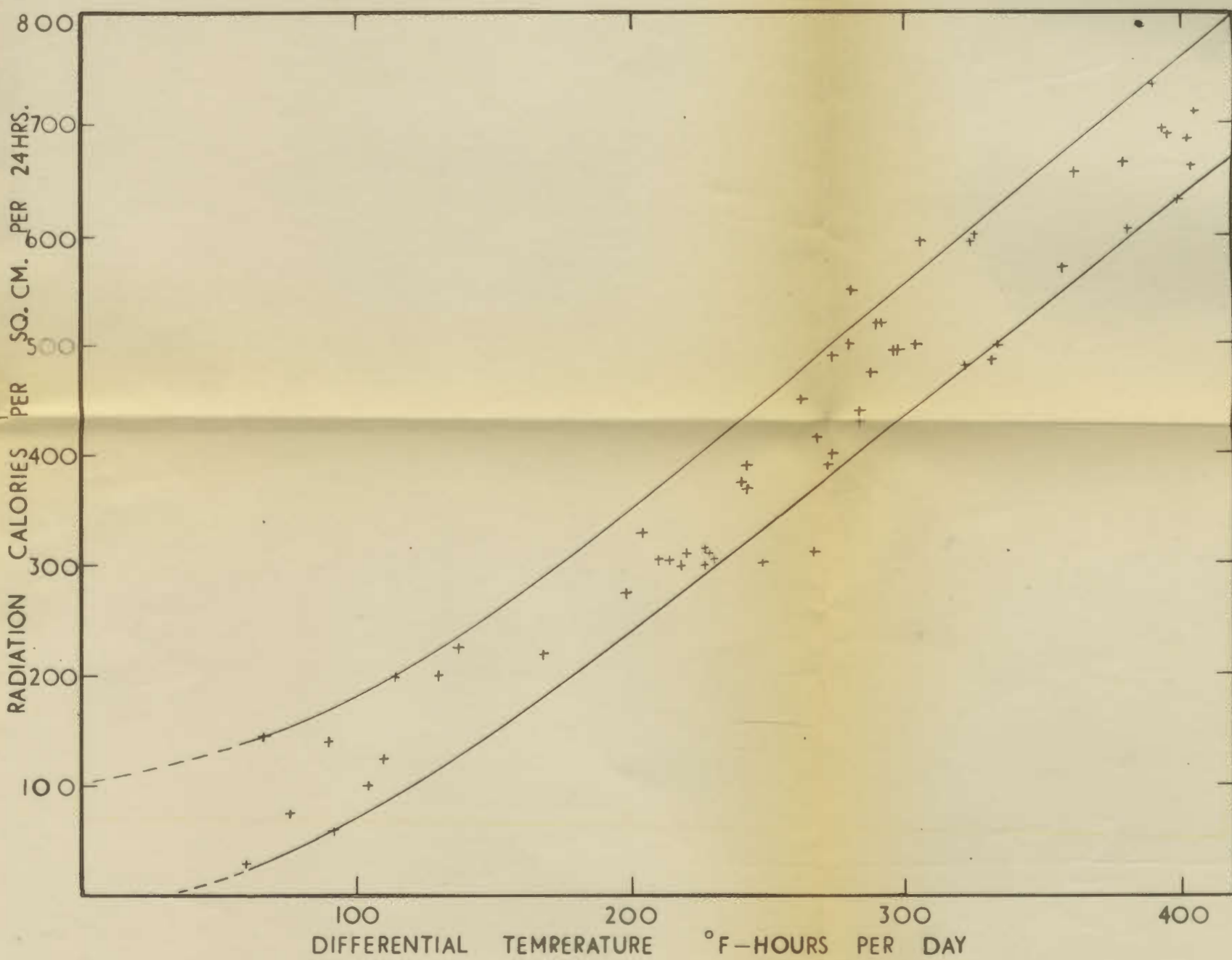DIFFERENTIAL TEMPERATURE

Figure 9b   VARIATION OF RADIATION WITH
DIFFERENTIAL TEMPERATURE

radiation was obtained at increased radiation intensity,
if it is assumed that temperature differential is a
resultant of radiation.

(ii)   From figure 9b it is seen that radiation
intensity does in fact determine the temperature
differential obtainable with simple air-cooled roof-
type solar stills.   The relation is not as regular as
in figures 7a and b or figure 9a but this is to be
expected since air temperature and winds are bound to
effect the issue

(iii)   The values plotted in figures 9a and b are
sufficiently regular to show that radiation intensity
largely determines the temperature differential and
that this in turn determines the distillate yield. The
importance of maintaining as high a differential
temperature as is practically possible, suggests that
artificial cooling of the condenser surface might be
advantageous.

B,2,(d). Effect of Temperature on Efficiency.   It has already been
pointed out that higher yields of distillate per unit of
radiation were obtained with increased radiation and that
increased radiation intensity were associated with higher
atmospheric temperatures.   Since the distillate yield per
unit radiation represents the thermal efficiency of a solar
still, it would appear that higher efficiencies were
obtained at increased atmospheric temperatures such as are
prevalent during summer.   Attempts were therefore made to
derive a mathematical relationship between radiation,
temperature and distillate yield, i.e. thermal efficiency
at various temperatures.

For calculation of the relative theoretical
efficiencies at summer and winter temperatures, the
following data, quoted under a and b of this subsection,
were used.   During summer the average bath temperature

was ...5

was 109.9°F and the average atmospheric temperature was 72.4°F resulting in a temperature difference of 37.5°F. The corresponding figures during winter were 93.5°, 60° and 33.5°F respectively. In order to evaluate only the effect of atmospheric temperature a mean temperature difference of 35.5°F was used for both summer and winter.

The rate at which distillation proceeds will obviously depend upon the vapour pressure difference between bath and condenser, and if it is assumed that the condenser temperature will be virtually the same as atmospheric, being in direct contact with it, then the vapour pressure difference may be calculated from the vapour pressure curve of water. It was thus found that the vapour pressure difference between bath and atmospherec (condenser) amounted to 41 mm. mercury in summer and to 29 mm. mercury in winter. The rate of evaporation should therefore be $\frac{41}{29}$ i.e. 1.41 times faster in summer than in winter for a similar temperature difference.

The higher rate of evaporation during summer does not necessarily mean that the thermal efficiency in summer was 1.41 times the winter value since a higher rate of evaporation must be accompanied by a higher rate of heat input if a constant temperature difference is to be maintained. A higher rate of evaporation at a constant temperature difference does, however, mean that a smaller proportion of the heat input is lost through conduction convection and reradiation, the latter being all dependant upon the temperature difference. This is demonstrated and evaluated in the following equations.

$$Q = C + \Delta pK\lambda + H \quad \dots\dots\dots\dots\dots(1)$$

where Q = Heat input into the bath per hour.

C = Heat lost per hour i.e. a constant
     at constant temperature difference.

Δp = The difference in vapour pressure

between .../

between bath and condenser.

K = The weight of distillate produced per hour per unit Δp.

λ = The latent heat of evaporation.

H = Heat absorbed per hour for increasing the temperature of the bath and its contents i.e. zero at equilibrium conditions.

The equation demonstrates that an increase in Δp must be accompanied by an increase in Q if the bath and its contents is not to cool down.

Thus $Q_W = C + \Delta p_W K \lambda$) suffixes w and s imply
$Q_S = C + \Delta p_S K \lambda$) winter and summer.

$= C + 1.41 \times \Delta p_W K \lambda$ since Δp_S was shown to be $= 1.41 \times \Delta p_W$.

i.e. $Q_S = Q_W + 0.41 \times \Delta p_W K \lambda$ .... (2)

In equation (1) the thermal efficiency of the still is the ratio of heat used for distillation to the total heat input.

i.e. Eff $= \dfrac{\Delta p K \lambda}{Q}$

It was found experimentally that the winter average of this ratio amounted to 28% (refer ... B, 1, observations 1 and IV)

Therefore $\Delta p_W K \lambda = 0.28 \, Q_W$ .... (3)

Now Eff. winter $= \dfrac{\Delta p_W K \lambda}{Q_W}$

and Eff. summer $= \dfrac{\Delta p_S K \lambda}{Q_S} = \dfrac{1.41 \, \Delta p_W K \lambda}{Q_S}$

i.e. $\dfrac{\text{Eff. summer}}{\text{Eff. winter}} = \dfrac{1.41 \, Q_W}{Q_S}$

$= \dfrac{1.41 \, Q_W}{Q_W + 0.41 \, \Delta p_W K \lambda}$ by substituting equat (2)

By .../

By substituting further equation (3)

$$\frac{Eff.s.}{Eff.w.} = \frac{1.41 \ Q_w}{Q_w + 0.41 \times 0.28 \ Q_w}$$

$$= \frac{1.41}{1 + 0.41 \times 0.28} = 1.2$$

An increase in atmospheric temperature from 60°F to
72.4°F should thus cause the efficiency at the latter
temperature to be 1.2 times as high as the efficiency at
the former temperature.

In actual fact the ratio of summer efficiency to
winter efficiency was found to be $\frac{0.529 x \lambda}{0.488 x \lambda}$ (refer $\text{II},B,1$
observation iv) i.e. = 1.08. This means that the
theoretically possible increase of thermal efficiency
at higher temperatures was not fully achieved in practice.
The reason must be sought in the fact that the condenser,
due to the poor conductivity of the glass, was not
maintained at atmospheric temperature, as was assumed for
the purpose of the above calculation.   The actual vapour
pressure difference was consequently much smaller than the
values used above, especially in summer when high radiation
intensities caused excessive heating of the glass condenser,
both through absorbed radiation and by the increased rate of
evaporation.   It was not possible to find any relationship
between condenser and atmospheric temperatures and it must
therefore be conceded that a theoretical relationship between
atmospheric temperature, distillate yield and radiation
cannot be derived.

The above calculations, serve to indicate that the
increased thermal efficiency observed at higher radiation
intensities is amply accounted for, by the rise in
atmospheric temperature which accompanies such higher
radiation intensities.

In order to assess whether any practical relationship
between atmospheric temperature and efficiency existed a
graph was plotted of distillate yield per unit radiation
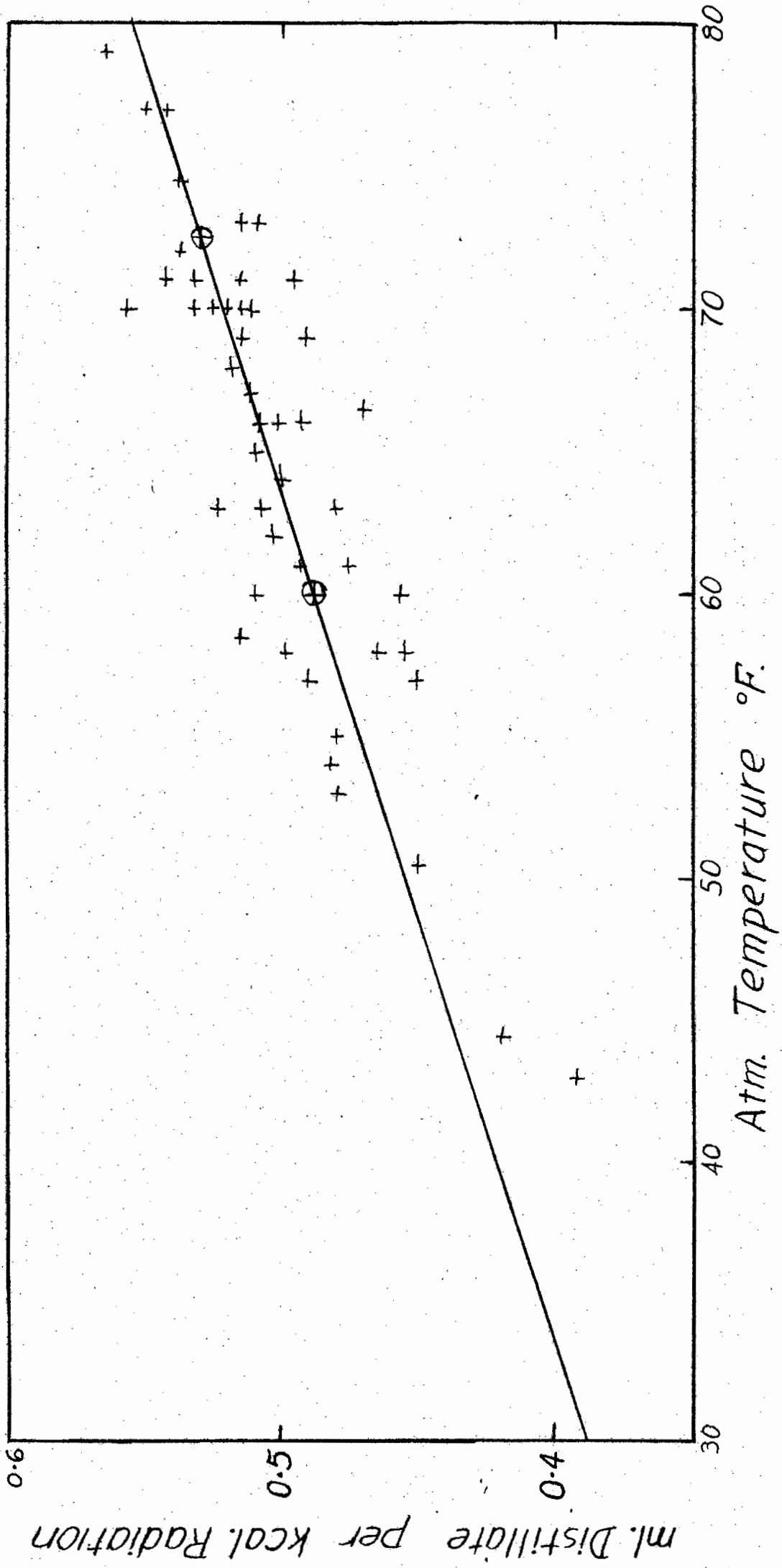
against ../

48.

Figure 9c. VARIATION OF DISTILLATE RATIO WITH ATMOSPHERIC TEMPERATURE

against atmospheric temperature - figure 9c.

It will be noted that no regular relationship existed. A straight line drawn through the points for average summer and winter values, nevertheless corresponds to an approximation of the individual values plotted. This straight line yields the following equation: ml. distillate per k.cal. radiation

$$= 0.40 + 0.0034 \text{ (temp }^{\circ}F - 32^{\circ})$$

$$= 0.40 + 0.0061x \text{ temp }^{\circ}C \dots\dots\dots\dots\dots\dots\dots(4)$$

This equation, being based on actual experimental results, implies that the observed increases in distillate yield per unit radiation received by the still were derived, solely, from increasing atmospheric temperature. It follows that horizontal straight lines would have been obtained in figures 7a and b if the temperature term of equation (4) were to be subtracted from the values actually obtained.

It should be noted that equation (4) does <u>not</u> correspond to the theoretical considerations. It would therefore be applicable only to stills of a design similar to the present experimental still. For the present experimental still the thermal efficiency may hence be expressed as a function of atmospheric temperature.

viz. $\text{Eff} = \dfrac{(0.4 + 0.0061x \text{ atm. temp }^{\circ}C \quad)x(20 + 574)}{10} \%$

This clearly demonstrates the important effect of atmospheric temperature upon the performance of solar stills of the present design.

B,3. <u>Effect of Winds, Rain, Humidity and Pressure.</u> During the run of the experiment, wide variations of all the above climatic phenomena were observed. It was not found possible to relate any of these with variations in yield of distillate apart of course from their indirect effect as manifested in temperature and radiation.

B,4. Insulation .../

B,4. Insulation of the Still

The main heat losses from the evaporation pan will occur through the base of the still, since this represents the largest area in direct contact with the pan. In order to ascertain the amount of heat lost in this manner, temperature records were taken at top and bottom of the 6" layer of vermiculite on which the pan rested. The quantity of heat conducted across the whole base during 24 hours was then calculated according to Fouriers Law being:

$$Q = \frac{kA\Delta t\theta}{L}$$

where k = coefficient of conductivity in BTU per sq.ft. per hour per ft. thickness per °F = 0.04 for dry vermiculite.

A = Total area of the base, 16 sq. ft.

L = base thickness, 6"

$\Delta t\theta$ = integral of time and temperature difference product as measured.

In table V such values are recorded together with the heat consumed by actual distillation.

TABLE V

CALCULATED HEAT LOSSES THROUGH BASE OF STILL

Date	$\Delta t\theta$ °F.hours	BTU lost through base	BTU Used for distillation	% Heat Lost per heat used
19/10/54	274	349	13,460	2.6
20/10/54	260	333	11,100	3.0
25/10/54 ✗	182	233	15,440	1.5
26/10/54 ✗	210	268	16,150	1.7
1/11/54 ✗	232	297	13,840	2.1

✗ Cooling of condenser surface employed

From table V it appears that the heat lost through the base of a well-insulated still is comparatively small. Expressed as a percentage of the heat utilised for distillation it amounts to about 2.5 while as a percentage of the total heat impinging on the still it is only 0.8.

It .../

It is however important to ensure low conductivity
in the base since it is directly related to the total
heat loss.   Thus, concrete with a conductivity of 0.5 BTU
per sq.ft. per hour per ft. thickness per $^\circ$F., would
theoretically cause 12.5 times the heat loss recorded
in table V.   It should further be noted that vermiculite
is specially prone to changes in conductivity from varying
moisture contents (1% increase in moisture content results
in a 10% increase in conductivity).   Since the vermiculite
used in the present still was subjected to occasional
condensate leaks and general humid conditions, the heat losses
as calculated in table V were considered to be deceptively
low.   In order to check the actual conductivity of the base
a heat-meter was subsequently fitted.   The meter used was a
standard thermopile plate as generally used by the National
Building Research Institute for measuring conductivity of
building components.   Flow of heat through the plate is
recorded in millivolts of E.M.F. difference between two
opposing thermocouples imbedded on opposite sides of the
plate.   The millivolt readings are then translated into
calories per sq. cm. per sec. by means of the calibration
factor of the meter.

By graphical integration of the rate of heat flow
with time, it was found that the actual heat lost per day
was of the order of 500 to 750 k.cal. or 2000 to 3000 BTU's
depdnding upon the temperature attained by the bath and the
duration of such elevated temperature.   This result indicated
that the actual conductivity of the moist vermiculite in the
still was about 10 times that of <u>dry</u> vermiculite.   Since it
would be extremely difficult and costly to ensure continuous
absence of moisture in the base of any still, it must be
conceded that vermiculite is not an effective insulating

material .../

material for the present purpose.

Lowered heat losses were incurred when the cooling of
the condenser surfaces resulted in the lowering of bath
temperature (refer C2 Observation (ii) below).

C. AUXILIARY EQUIPMENT

C.1. <u>Mirrors</u>.   Placing a vertical mirror of $\frac{1}{2}$ the size of
the evaporating pan (see II,A,3 of this Chapter)
along the south side of the still should theoretically
increase the radiation on the still by 44% of the
original value when the angle of incidence is 40° i.e.
at midwinter.   In midsummer the incidence of radiation
is about 87° which should give a 2% increase.   With the
mirror fixed in one position (figure 4) the total reflected
radiation impinges on the still, only at midday.   During
the rest of the day part of the reflected radiation is
lost.   In summer a vertical mirror is of course, very
much less efficient, but the angle of the mirror was
purposely not adjusted since it was considered that such
changes would complicate, practical operation unduly.

The average increase of radiation resulting from
such a fixed mirror should thus be 23% but owing to
inefficient reflection it was estimated to be 18% of the
radiation normally received by the still.   A corresponding
increase in distillate yield per unit of normal radiation
intensity, may be expected, but comparison with distillate
yields during a corresponding period when the mirror was
not in use, indicated that this was not attained.   In table
VI the ratio of distillate to radiation is recorded together
with actual distillate yields.

TABLE VI ...../

TABLE VI

DISTILLATION WITH AN ADDITIONAL MIRROR

Date of Period Ending	Average Daily Radiation Cal/cm^2.	Distillate yield ml.	Ratio of Distillate Radiation ml./kcal.
18/7/54	360	3050	0.571
25/7/54	380	3030	0.536
1/8/54	385	3230	0.564
8/8/54	426	3690	0.583
15/8/54	386	3330	0.581
22/8/54	419	3600	0.578
29/8/54	464	3840	0.556
6/9/54	481	3980	0.557
12/9/54	490	4300	0.591
19/9/54	387	3100	0.538
26/9/54	453	3920	0.582
3/10/54	447	3740	0.563
11/10/54	526	4500	0.575
17/10/54	521	4600	0.598
24/10/54	513	4260	0.558
31/10/54	465	3850	0.557
7/11/54	541	4600	0.572
14/11/54	543	4600	0.568
21/11/54	557	4600	0.556
28/11/54	654	5320	0.547
5/12/54	581	4740	0.549
12/12/54	453	3800	0.564
19/12/54	658	5440	0.555
27/12/54	561	4600	0.552

Overall average ratio   =   0.565 ml/kcal.
Ratio for corresponding period without mirror   =   0.523 ml/kcal

The average ratio for the period 15th July to 27th December was 0.565 and 0.523 ml/kcal. with and without the mirror respectively, i.e. an 8% increase.   There was no significant difference in the average atmospheric temperatures for the two periods which meant that the increased ratio was affected by the mirror only.

This increased ratio was incompatable with
the increased radiation received by the still. The
reason may be sought in the fact that the southern
side of the still, normally remained relatively cool,
thus acting as an efficient condenser. With the
mirror in position the south facing glass was heated
and consequently condensation was more difficult. It
is therefore clear that the use of mirrors without
provision of additional cool condenser surface is not
to be recommended.

C,2. Cooling of Condensing Surface. As was indicated
previously provision of a cooled condenser would
accelerate distillation. In order to assess the value
of such cooling, water was sprayed over the south-facing
side of the cover in an even thin layer, continuously
from 8 a.m. to 4 p.m. The temperature of the condensing
surface was recorded at regular intervals. The results
are recorded in table VII while figure 10 depicts typical
temperature variations.

TABLE VII

DISTILLATION WITH A COOLED CONDENSER SURFACE

Date	Total Daily Radiation cal/sq.cm.	Distillate yield ml.	Ratio of Distillate to Radiation.ml/kcal.	Weather Conditions.
25/10/54	566	6500	0.768	Slight cloud and wind.
26/10/54	662	6900	0.704	-do-
1/11/54	613	5830	0.642	cloudy - no wind
8/11/54	701	6500	0.624	slight cloud and wind
9/11 /54	394	4000	0.683	cloudy with rain
10/11/54	478	5400	0.759	-do
18/11/54	685	6700	0.658	slight cloud and wind.
Average ratio	=	0.691	ml/kcal.	

Observations:

(1)   The average ratio of distillate and radiation during
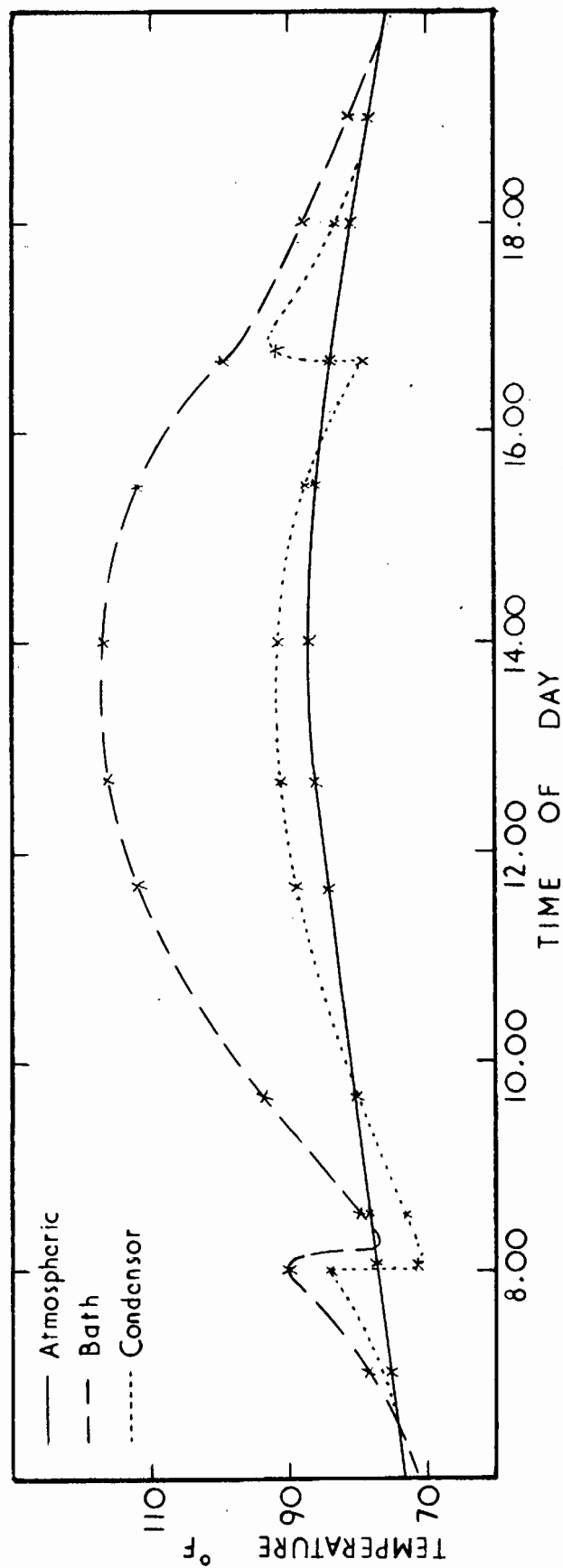the period 25/10/54 to 18/11/54, without cooling was/......

Figure 10 TEMP. CHANGES WITH COOLED CONDENSOR

was 0.563 ml/kcal. (refer table VI), as compared with 0.691 ml/kcal. when cooling of condenser surface was employed. This represents a 23% increase.

(ii)   The temperature of the bath dropped sharply when cooling was commenced and remained about 20°F. less than usual throughout the period when cooling was continued.   This indicates that more rapid evaporation occurs and the resultant lower bath temperature is advantageous since lower heat losses must result.   (Refer Table V).

(iii)   The low thermal efficiency of a solar still, is obviously due to various inherent heat losses.   The chief advantage of a cooled condenser surface therefore is to minimise these losses by producing a lowered bath temperature.

(iv)   The temperature of the condenser (measured on the inside surface) dropped sharply when cooling commenced and remained close to atmospheric throughout.

(v)   Spraying water over the glass surface attenuates penetration of radiation and consequently causes a lowered heating effect.

(vi)   On the whole the advantages to be gained from water cooling of condenser surfaces does not weigh up against the cost and practical difficulties involved.

(vii)   The use of a separate flat plate solar water heater coupled to a cooled condenser may prove advantageous and should be investigated further.

D.   DISCUSSION.

The present experiments have shown that solar distillation can, under South African conditions, be applied successfully for production of potable water.   The results provide much needed data regarding the performance of such stills.   These data form a useful basis for comparison with similar work, subsequently done elsewhere and can be applied

directly.../

directly for practical solar distillation in South Africa.

D1. <u>Results of the Investigations</u>

The operation of an experimental solar still for a period
of more than 2½ years had not previously been undertaken. The
present investigation therefore provides the most extensive
record of the performance of such stills in relation to extreme
climatic conditions, such as are prevalent in South Africa. It
was further possible to iron out design and operational
difficulties which would confront prospective users of the
process.

Important findings of the work were the following:-

D,I,(a). <u>Efficiency of Solar Radiation Utilisation</u>. Correlation
of distillate yield with solar radiation, measured at the
site, indicated that an average of 30% of the total radiant
energy impinging on the still was used for distillation. More
than 2/3 of the available energy was thus lost. It was not
possible to determine the exact manner in which this loss was
incurred, but as was pointed out under II,B,4 of this chapter,
the poor insulation of the still caused a loss of at least 8%
of the incident radiant energy. It is probable that absorption
and reflection of radiation by the glass canopy accounted for
a 20% loss, while reradiation from the pan accounted for another
10 to 20%. Shadows cast by the canopy framework and re-
evaporation of distillate will cause additional losses.

Most of these losses are inherent in the design of single-
stage non-focussing solar distillers and cannot be overcome
easily. The relatively low efficiency of utilisation of solar
energy should, however, be viewed against the extreme simplicity
of the apparatus. Higher efficiencies will no doubt be
attainable with more elaborate designs, but, since solar energy
is free and abundant, there is obviously not the same instigus
for high efficiency as with fuel operated plants. In order to

obtain ...

obtain a simple, cheap and practically workable apparatus,
therefore, an efficiency of 20 to 35% must be accepted.

D,1,(b). Influence of Climatic Factors.

(i) Temperature. The important effect of atmospheric
temperature upon the performance of solar stills was
demonstrated under item II,B,2,d of this chapter.   It was
pointed out that higher thermal efficiencies were obtained
at increased temperatures.   Atmospheric temperature of
course cannot be controlled but the experiments showed that
suitable yields of distillate may be expected in all moderate
climates.

(ii) Humidity of the atmosphere should not affect the
operation of a solar still, since the structure is such that
ambient air is specifically excluded from the apparatus.
Variations of from 30 to 90% relative humidity had no effect
on the efficiency of distillation.

(iii) Barometric Pressure. Variations of atmospheric
pressure, within the limits generally encountered, did not
affect operation of the experimental solar still.

(iv) Winds.   An exact record of wind velocities was not
taken but it was observed that strong wind, 10 to 15 knots,
caused a decrease in the heat efficiency of the still (Refer
table III).   This is contrary to what may be expected since
wind should theoretically lower the temperature of the glass
condensing surface and hence improve the distillation.   The
lowered efficiency, actually obtained, must therefore be
attributed to possible deleterious effects of ambient air
movement.   The most likely of these effects are increased
heat losses and the passage of air currents through the still
due to inadequate sealing of the apparatus (refer II,A,4,b. of
this chapter).

In.../

In practice it would be difficult to construct a completely heat insulated and draught-proof apparatus and it must therefore be accepted that the theoretical advantage of winds will generally be annulled. On the other hand, however, wind should have no detrimental effect on a properly constructed solar still.

(v) <u>Rain</u>. Intermittent showers on a heated still caused temporary rapid distillation by virtue of its cooling of the condensing surface. On the whole, however, it reduced distillation indirectly via the obstruction of solar radiation. Since solar distillation will never be used in rainy areas, the effect of rain requires no further consideration.

D,(c). <u>Insulation of the Still</u>.

As was pointed out under II,B,4 of this chapter, the actual amount of heat lost through the base of the experimental solar still was about 10 times as high as the calculated value, the actual loss thus amounting to about 8% of the incident radiant energy. This stressed the importance of providing adequate insulation of the base of solar stills, but it also proved that solar stills will operate even under adverse conditions such as with really poor insulation.

According to the calculations under II,B,4 of this chapter, the heat loss might well be reduced to less than 1% by supporting the bath of the still on a 6 inch thick layer of moisture resistant insulating material with a conductivity of less than 0.05 B.T.U. per sq. ft. per hour per ft. thickness per °F. (It should thus be possible to increase the heat efficiency of the still to at least 37%). A suitable material for insulation will be "slag wool" or glass wool, but alternatively the base of the still may be built of "concrete foam" insulating bricks on which is supported a waterproof pan.

D,(d). <u>Heat Storage</u>. A considerable proportion of the radiant heat absorbed by the still was used for heating the bath and its contents (refer II,B,2,a,iv of this chapter). Calculations show that, on the average, 20% of the incident solar radiation was used

for ../

for heating the saline water contained in the bath.   In
addition, the bath itself and the body of the still required
to be heated.   This thermal capacity of the still constituted
a heat ballast which abated the peak temperature attained by
the bath and hence to a limited extent, the efficiency of
the still.   It did not, however, constitute a direct heat
loss, since it provided a supply of sensible heat for
distillation when solar radiation declined.   It was thus
observed that distillation always continued long after sunset.

In order to utilise stored heat effectively adequate
thermal insulation of the still is essential.   In practice,
perfect thermal insulation cannot be obtained (refer item c
of this sub-section) and hence a portion of the sensible heat
will necessarily be lost.   The thermal capacity of a solar
still should therefore be limited to a value, commensurable
with technical workability.   This aspect of solar still
design is dealt with further under item g,iv of this sub-
section.   In general, however, it may be accepted that the
better the insulation, the higher may be the thermal capacity
of the still.

D,I,(e) Practical Difficulties.

The experiments focussed attention on various
pitfalls which must be gaurded against.

(i) Sealing the still.   Even the most careful workman-
ship will leave cracks and crevices, especially in the canopy,
through which air leakage will occur.   It is therefore
necessary to seal all joints with a non-hardening caulking mate-
rial while temporary joints at inspection covers should be
sealed with sponge rubber strips.   In addition, every care
should be taken to ensure a draught-tight seal between the
canopy and the bath of the still.   In practice it would be

convenient ../

convenient to construct the bath and the canopy separately
and the two units should then be bolted together with a
sponge rubber gasket.

(ii) <u>Collecting the condensate</u>. It is of primary
importance that all condensate should be delivered into the
collecting troughs. The thin film of condensate which
trickles down the inside surface of the glass canopy is
not easily severed from the glass and will penetrate the
smallest crevice (refer II,A,4,a, of this chapter). It is
therefore important to ensure that the lower edge of the
glass panes rests within the distillate collecting trough.
Alternatively, distillate deflectors such as are shown in
figure 6 may be used.

(iii) <u>The Transparent surface</u>. The transparent
condensing surface should have a high diathermancy, good
wettability and strength. The use of transparent plastic
sheet may seem attractive since it could be moulded to
shape, but at present its use would be unpracticable on
account of several undesirable properties viz., high cost,
low resistance to weathering and surface damage, and poor
wettability. In the present experiments, glass panes mounted
in a rigid frame were found to be very suitable. It
required only external cleaning to prevent opacity due to
dust and dirt. The frequency of cleaning depended on the
amount of wind and dust, but as a general rule, it was
required every second or third day.

D,l,(f). <u>Auxiliary Equipment</u>.

The investigations showed that the use of auxiliary
equipment to aid distillation, such as mirrors and water-
cooled condensers, would somewhat increase the efficiency of
the still. The increase, however, was not commensurate with
the extra cost and trouble involved.

g) .../

D,1,(g). Recommendations regarding construction.

The present experiments served as a guide to
optimum practical construction of solar stills.   As
was pointed out under item (a) of this subsection, the
primary considerations in constructing solar stills
should be simplicity, economy and workability while
efficiency of heat utilisation should receive secondary
consideration.   Such single-stage non-concentrating
solar distillers can, if necessary, be constructed by
individual householders provided that the following
basic requirements are observed:-

(i) The size of unit to be used should be calculated
according to the formula given below under sub-section 3.

The still should not be wider than 4 to 5 feet since
increased width increases the distance from the bath to
the apex i.e. the distance through which water vapour
must diffuse, and hence it decreases distillation.
Increased area of still should therefore be sought via
increased length.

(ii)   The surface of the bath in which the salt water
is to be contained must be perfectly level so as to prevent
island formation at low water depths.

(iii) The bath should not be deeper than 3 inches if
the sides are not to obscure low incident radiation unduly.

(iv)   The depth of salt water must be sufficient for
at least one day's operation without replenishing.   If the
salt water in the pan is replenished only once per day at
sunrise, there is no heat loss incurred through discharge
of partially-concentrated brine since the bath and its
contents are then at their minimum temperature (refer II,B,
2,a,iii of this chapter).   The experiments have shown that

evaporation from the bath will generally not exceed $\frac{1}{5}$ inch per day and that a safe working depth for a day's operation is around $\frac{1}{2}$ inch.

The use of increased depths of liquid which will require less frequent replenishing seems attractive, but adds to the heat capacity of the unit.(Refer item d of this sub-section). It is therefore recommended that the depth of liquid in the bath should be limited to a value which will allow unattended operation of the still for 3 or 4 days, at which intervals dusting of the glass panes will in any case be required.(Refer item e,iii of this sub-section). Experience has shown that a liquid depth of 1 to 1.5 inches is satisfactory for this purpose.

(v) The bath should be painted jet black with a water-proof, temperature and corrosion resistant paint. A synthetic plastic paint was found most suitable.

(vi) The bath should be well insulated. For this purpose, the recommendations under item c of this sub-section should be followed.

(vii) The canopy should be made of light steel or aluminium, either to be of narrow section so as to cast a minimum shadow and yet strong enough to provide a rigid structure. It should snugly fit the base of the still so as to ensure a draught-tight seal. The longitudinal sides should slope at an angle of 40° to 45° to the horizontal and should project into the distillate collecting channel.(Refer e,ii of this subsection).

The longitudinal sides of the canopy can conveniently consist of standard steel window frames. The angle of slope and/or the width of the bath may then be adjusted slightly to accommodate a standard 3 feet size. The triangular end pieces of the canopy will of course have to be made to

measure ../

(viii) Glass panes $\frac{3}{16}$" thick should be puttied in the frame of the canopy after the whole still has been assembled.   Thinner glass would increase the efficiency of the still but render it more vulnerable.

(ix)   The whole apparatus should be orientated so that its longitudanal axis points due east-west.   In this manner the still will receive a maximum amount of sunshine.

D.2. Comparison with Results obtained Elsewhere.

Reports on experimental solar distillation carried out in the United States of America became available after completion of the present investigations.   Telkes (46) reported in 1953 on development during World War II of a portable inflatable type solar still, suitable for life rafts. She also gave some results of experiments conducted with small inclined plate solar stills and computed heat balances for the two types.   The tests were carried out at Cambridge Mass., 42°N. latitude.   Howe (47) reported on experiments conducted at San Francisco 38°N. latitude, with several large (51' long) inclined plate solar stills.   Rounds (48) recorded the operation of several inclined plate solar stills at the Virgin Islands 18°N latitude.

It is not possible to compare distillate yields obtained by these workers, directly with the present findings since climatic conditions at the three centres vary widely from those prevalent in South Africa.   Solar radiation, for instance, at Cambridge and San Francisco is less than in South Africa on account of their latitudes (refer table VIII). In the Virgin Islands again, it is rather similar but unfortunately no record of solar radiation was taken there, the values used having been interpolated from observations made elsewhere.   The following correlation of results can nevertheless be made:-

(a) ../

D.2.(a). Efficiency.   Telkes states that the heat efficiency
of a single effect inclined plate solar still may approach
70% and found experimentally that this efficiency was
obtainable with solar radiation values of 300 B.T.U.'s per
sq. ft. per hour (81 cals per sq. cm. per hour).   Her
findings are apparently based on observations made at midday
only, and are therefore of little value for continuous
operation of solar stills.   It is interesting to note,
however, that higher efficiencies were obtained with
increased solar radiation.   Similar observations were made
during the present investigations (refer figure 7b) but it
was concluded that this was due to the higher atmospheric
temperature which accompanied radiation intensity.

Rounds reported the efficiency of solar stills, which
were constructed according to Telkes' design, as being
around 36%.   It would therefore seem as if the high
efficiencies claimed at first did not materialise.   An
efficiency of 35% is in agreement with the present findings.
The work undertaken by Howe resulted in an efficiency of
solar radiation utilisation of 24.9% which is rather lower
than the value of the present study.   However, none of
these workers evaluated the effect of atmospheric temperature.
It might well be, that the lowered efficiency obtained by Howe
was primarily due to the lower average atmospheric
temperature, 56°F, at San Francisco while the higher
atmospheric temperature of the Virgin Islands, 75°F
accounted for the slightly higher efficiency reported by
Rounds.

It is thus concluded that the heat efficiency obtained
in the present experiments, an annual average of 30%,
represented a fair average of what will be attained in

moderate .../

This conclusion cannot be accepted without reservations because the heat absorbed by the water in the bath cannot simply disappear. It can be lost only by conduction and/or re-radiation, for which separate allowances are made in the heat balances computed by the former workers. The argument offered under 1d of this section would therefore seem more acceptable viz. that increased heat capacity of the still limits the overall efficiency mainly by decreasing the temperature attained in the bath.

The latter conclusion was later affirmed by Löf (49) who suggested that large solar stills, covering several acres of ground, might be constructed flat on the ground without special insulation so as to utilise the earth for a heat storage reservoir. The heat conducted into the ground would then be stored and reverted to the still at night time. Only a relatively small heat loss is expected at the perimeter of such a large still.

D,3. <u>Practical Utilisation of Solar Distillation</u>

The present investigations have shown that solar distillation is primarily a function of radiation intensity and that it can be applied successfully wherever sufficient radiation is available provided that certain structural requirements are complied with. The essential requirements for construction of solar stills have been outlined under 1,g of this section. The latter recommendations were based on data and experience obtained with the present experimental still and their soundness was subsequently confirmed by reports of other investigators. It therefore now remains to derive a formula for expected distillate yields at various localities.

Theoretically, any quantity of water can be distilled anywhere, provided that the area of solar still is large enough to collect sufficient radiation. In table IV it

was ...../

was recorded that 0.505 ml. of distilled water was produced per kilocalorie of solar radiation received by the still and it was suggested under 1,a of this section above, that it might well be increased to 0.584 ml./kcal.—35% efficiency, with improved thermal insulation.   When the latter value is used for calculating the size of still required for a given locality, equation (4) under II,B,2 d of this chapter should be amended as follows:

ml. distillate/kcal. radiation $= 0.48 + 0.0061 \times$ temp^{o}C.

Then, with a radiation of R kcal. per sq. cm. per day and a temperature of T^{o}C the distillate produced

$$= (0.48 + 0.0061T)R \text{ ml. per sq. cm. per day} \quad \ldots\ldots(5)$$

If it is desired to produce x ml. distilled water per day the size of still required

$$= \frac{x}{(0.48 + 0.0061T)R} \text{ sq. cm.} \quad \ldots\ldots\ldots(6)$$

In equations (5) and (6) the values of R and T will vary from place to place.   Approximate values may be obtained from consideration of the position on the earths surface, as follows:-

According to Milankovitch, quoted by Drummond (50) the radiation reaching the earth's outer atmosphere may be calculated from the formula:

$$\text{Daily Total Radiation} = \int_{t_1}^{t_2} \frac{I_0}{r^2} \cos Z \, dt.$$

where t_1 = time of sunrise

t_2 = time of sunset

r = radius vector of the earth

z = the zenith distance

I_0 = the solar constant i.e. 2.00 cal/sq. cm./min.

Some of this radiation is absorbed and scattered in the earth's atmosphere and the exact proportion which ultimately reaches the earth's surface is dependent upon

the ..../

the humidity, turbidity and to some extent the CO_2 content
of the atmosphere. Drummond found that over Southern
Africa an average of 61% reaches the earth's surface which
is rather higher than for Europe, North America or the
East Indies. Assuming a transmission factor of 0.6, the
total daily radiation received at the earth's surface may
be obtained/ in kcal. per sq. cm. from the above equation by
introducing the factor $\dfrac{0.6}{1000}$

then $R = 0.0006 \times \displaystyle\int_{t_1}^{t_2} \dfrac{2.0}{r^2} \cos Z \, dt$ ....(7)

Atmospheric temperature also varies with the cosine
of the sun's zenith distance. From consideration of world
isotherms it was postulated that the day temperature is
represented by the equation: $T°C = 50 \times \cos Z - 20$ ...(8)

On an annual average the value of Z in both equations
(7) and (8) will be equal to the latitude. It is thus
possible to evaluate R and T and hence the performance of
an inclined plate solar still, simply from a knowledge of
the ordinates of a particular site. The values of both
R and T will obviously decrease with latitude and from
equation (6) it is clear that such decrease will involve an
increase in the size of still required. The size of still
required, determines its cost, and hence it was calculated
that the cost of solar stills to be used at latitudes greater
than $40°$ would be excessive.

Note: The values of R and T will generally be more
conveniently and accurately interpolated from records of
surrounding meteorological stations. Such data is contained
in table VIII, which is reproduced by courtecy of Mr. A.J.
Drummond (50).

TABLE VIII

Total Annual Radiation received on a horizontal plane

Country	Station	Latitude	Longitude	Height above sea level in ft.	Radiation in kcal/cm^2		
					Summer	Winter	Annual
Union of South Africa	Pretoria	25°45'S.	28°14'E.	4490	101.4	73.1	174.5
	Bloemfontein	29°07'S.	26°11'E.	4664	94.5	67.7	162.2
	Cape Town	33°54'S.	18°32'E.	56	112.1	55.7	167.8
South West Africa	Windhoek	22°34'S.	17°06'E.	5700	109.7	87.0	196.7
Kenya	Nairobi	1°16'S.	36°48'E.	5970	102.4	75.9	178.3
U.S.A. East	Washington	38°56'N.	77°05'W.	397	79.5	38.9	118.4
West	Riverside (Cal.)	33°58'N.	177°28'W.	1051	95.7	53.9	149.6
Central America	Mexico City	19°24'N.	99°06'W.	7585	85.3	77.4	162.7
Sweden	Stockholm	59°17'N.	18°03'E.	Near S.L.	62.2	13.0	75.2
United Kingdom	London	51°28'N.	0°19'E.	18	70.8	16.3	87.1
Germany	Berlin	52°23'N.	13°04'E.	197	65.9	17.9	83.8
Switzerland	Zürich	47°23'N.	8°23'E.	1620	74.4	26.2	100.6
France	Nice	43°44'N.	7°14'E.	60	95.0	38.2	133.2
Java	Batavia	6°11'S	106°50'E.	26	69.8	71.9	141.7

70.

D,4. <u>The Cost of Solar Distillation</u>

The cost of solar distillation is almost wholly that of redeeming the capital cost of construction. The amount of labour required for cleaning and replenishing of saline waters on moderately sized stills such as will be required by individual households, will be negligible. It will probably be performed as part of other routine duties.

The cost of construction will obviously depend upon the facilities available to prospective users. For the purpose of the following calculations it is assumed that a still of 4' x 20' is required by a household and that it can be constructed on the site. The total cost will be composed of the following items:

D,4,(a). <u>The evaporator bath</u>, with distillate collecting troughs on the sides, may be constructed of concrete, 3" thick and supported on a suitable insulating layer 6" thick. About 1 cubic yrd. of concrete and two cubic yrds. of insulating bricks would thus be required. With building and finishing costs added the bath should cost about £15.

D,4,(b). <u>The Canopy</u>. Standard window frames 3' x 3' may be used for the longitudanal sides of the canopy. Fourteen such windows will be required and two triangular windows at the ends will have to be specially made. With assembly the canopy should cost about £50.

D,4,(c). The pan must be painted with several layers of waterproof, plastic, paint and the rest of the apparatus also requires paint protection against corrosion. In addition sponge rubber gaskets, water inlets and outlets and various other contingency items will be required. These might well add up to £10.

The total cost of an eighty sq. ft. solar still would thus amount to about £75 or just less than £1 per sq. ft.

Under .../

Under average South African conditions, refer table VIII
and equation (5) above, a still of 80 sq. ft. will produce
about 5 gallons of distilled water daily i.e. about 1800
gallons annually.　　Interest and redemption of the capital
involved would amount to £6 per annum or about 4 pence per
day.　　This cost might seem high when counted against
gallons of water produced but as an individual item of cost
of living, it is certainly within the scope of any normal
household.

The volume of potable water obtainable from a solar
still may be increased by admixture with natural saline water
to yield a larger volume of potable water of low salinity.
The troublefree, simple operation of a small solar still
and the fact that it operates best during dry sunny weather,
further enhance its attraction.

C H A P T E R 3.

D E F L U O R I D A T I O N.

As was indicated previously a practical method for
defluoridation of water supplies is urgently needed in many
parts of South Africa and elsewhere.   Soon after the disco-
very that dental fluorosis was caused by excess fluorides in
drinking water, methods were devised for removal of such
fluoride and numerous alternative or improved methods have
been suggested from time to time.   Nevertheless, at the
present time, very little practical application has been made
of any of these methods on account of their high cost and the
complexity of the operating procedures.   In cases where
fluoride concentrations above 1.5 p.p.m. occur it has gene-
rally been more economical to develop alternative sources of
supply, of low fluoride concentration.   In South Africa water
supplies are limited and the need for defluoridation of
fluoride-containing waters is accordingly more urgent.

Fluoride may be removed from water by adsorption on
various flocculent precipitates or by ion exchange.   Such re-
moval must, however, be selective since the extremely low
residual fluoride concentration required would otherwise entail
almost complete demineralisation, and removal of all mineral
constituents would very soon exhaust the exchange media.
Fluorides generally occur in fairly saline water, 1000 to 2000
p.p.m. salinity and combined removal of all mineral constituents
is therefore uneconomical and unwarrented.   During the course
of the present investigations the most promising of the various
defluoridants suggested in the literature, were evaluated.   It
was found that most of them did not meet the claims made, while
their preparation was cumbersome and costly.   An additional
large number of preparations were tested experimentally and it
was observed that phosphatic materials were superior defluori-

<div align="right">dants .../</div>

dants. X-ray diffraction analysis of the latter indicated that high defluoridising efficiency was associated with apatite crystal formation. A preliminary report on this finding has already been published (51). The crystal structure of apatite had previously been studied by Beevers and McIntire (52) who concluded that the structure was such that it would accommodate fluoride and hydroxide ions only. The latter study, together with the present experimental findings focussed attention on apatite as a selective exchange medium and the major part of the work was consequently devoted to development of a suitable apatite material.

Attempts to produce apatites from a cheap and readily available raw material, led to the discovery that superphosphate of lime could be converted into a microcrystalline apatite by simply treating it with an excess of a dilute solution of sodium hydroxide. Macro apatite crystals, obviously do not provide sufficient surface area, thence the preliminary degradation of rock phosphate to superphosphate was essential.

As a result of this work it was possible to develop practical methods for defluoridising both communal and household quantities of water. A large-scale plant was subsequently designed and put into operation at the Horticultural Research Station near Pretoria, South Africa.

I. M E T H O D S O F F L U O R I D E A S S A Y.

In order to assess the efficiencies of various defluoridants, an accurate method of analysis was required. The various methods which have been described, depend generally upon the fading of coloured complexes caused by fluoride combination with a constituent of the former. The various methods may be grouped under (a) direct methods of analysis and (b) methods involving the distillation of the fluoride from the original water sample.

A. Direct Methods../

A. DIRECT METHODS.

Several organic dyes form coloured lakes with
thorium and zirconium but these metals also form slightly
ionized compounds with fluoride. The colour intensity of the
lake is thus reduced by the presence of fluoride and the amount
of fading measures the quantity of fluoride present.

The suitability of some 200 dyes as indicators for
the titration of fluoride with thorium nitrate was investigated
by Willard and Horton (53). The best colorimetric indicators
found were, in order of effectiveness, purpurin sulphonato,
Alizarin Red S., eriochromcyanin R, dicyanoquinizarin and
chrome azural S. The best fluorescent indicators were, pure
sublimed morin and quercitin.

Fluorides will also reduce the colour of ferric
thiocyanate by virtue of the complex formation between ferric
and fluoride ions. A method for determining fluoride by
application of this principle has been described by Foster (54).
The amount of fading was measured colorimetrically and allowance
for interfering elements [+] such as sulphate, chloride, nitrate
and borate was made graphically. The method has been severely
criticised by Doruff and Abbott (55) because there is apparently
no constant relation between the amount of ferric and fluoride
ion combined in the complex.

The use of alizarin Red S. either alone or in
combination with zirconium, as an indicator for the titration
of fluoride with thorium has been applied most generally.
Several workers have investigated the implications of this method
and have suggested means for overcoming the interference caused
by foreign ions.

De Boer (56) and later Pavelka (57), Feigl (58) and
Alamarin (59) determined fluorides colorimetrically by the use
of zirconium-alizarin mixture, the colour of which faded in the
presence of fluoride. Willard and Winter (60) found that the

[+] Note: Any ion which forms a precipitate   slow .../
or a nondissociated salt with fluoride
or with the titrant interferes with the titration.

slow rate of reaction between zirconium and fluoride caused
the results to be inaccurate.   These workers suggested the
use of thorium nitrate to combine with the fluoride, the
zirconium-alizarin mixture then indicating the end point of
the titration.   The titration was carried out in a 50% ethyl
alcohol solution to prevent dissociation of thorium fluoride.

Thompson and Taylor (61) boiled the mixture of
zirconium and alizarin with the fluoride sample in order to
accelerate the reaction between zirconium and fluoride. The
interfering effect of sulphate and chloride was compensated
for by addition of similar quantities of these ions to the
standards used for comparison.   Sanchis (62) developed this
method for use with natural waters but did not succeed in
eliminating the effects of interfering ions completely.

In order to minimise interference, Reynolds & Hill
(63) used a buffer to control the pH of the titrated solution
at about 3.1.   At this pH, plain alizarin dye was found
suitable as an indicator, with a greater sensitivity. (Previously
the use of zirconium-alizarin mixture was essential because the
simplified indicator was too sensitive to changes in pH).
These workers also found that the titration of fluoride with
thorium nitrate may be carried out in aqueous solution (without
addition of ethyl alcohol) with a resultant sharper end point
and no excessive error.

A further modification of the latter procedure (63)
was described by Stevens (64).   This method provides for a
simplified rapid determination of fluoride by eliminating the
use of a large number of standards for colour comparison.

According to this method fluoride is titrated in
aqueous buffered solution with thorium nitrate to a standard
pink colour, using plain alizarin indicator.   The same quantity
of thorium is then titrated with standard fluoride solution to
a matched colour intensity in another tube.   Half neutralised,

normal monochloracetic acid is used as a buffer, maintaining
the pH of the solutions at 2.8 where interference from foreign
ions, except sulphate, is claimed to be at a minimum.   To
compensate for sulphate interference an equivalent quantity
is added to the back titration.   It is thus necessary to
first determine the sulphate content of the sample.   During
the present investigations this method was found to be very
suitable for routine determination of the fluoride in large
numbers of water samples with constant sulphate concentration.

The method of Stevens (64) was critically reviewed
by Copeman (65) who compared it with the standard distillation
and colorimetric methods.   Reproducible results were obtained
and the recovery of added fluoride was also satisfactory.

In the course of the present studies, spectrophoto-
metric comparison of colour intensity was found unsatisfactory
due to slight turbidity which sometimes occurred in the sample
tube on addition of thorium nitrate.   Visible comparison,
however, was found suitable since addition of 0.5 ml. standard
fluoride solution representing 0.05 p.p.m. of fluoride ion gave
a distinct colour change.

Some analytical results are given in Table IX.

TABLE IX

ACCURACY OF FLUORIDE DETERMINATIONS

Fluoride addition to tap water(p.p.m.)	Total F^- found (p.p.m.)
Nil	0.2
0.5	0.65
1.0	1.1
2.0	2,0
3.0	3.05
4.0	4.0

It was noted that fluoride recovery was influenced by changes in pH during titration as indicated in Table X.

TABLE X.

EFFECT OF pH ON FLUORIDE RECOVERY

Fluoride addition to tap water (p.p.m.)	pH of Tube	F⁻ found (p.p.m.)
Nil	3.2	- 0.1
Nil	2.95 ✕	0.08
Nil	2.75	0.4
2.5	3.15	2.1
2.5	3.0 ✕	2.7
2.5	2.75	3.8

✕ Alkalinity of sample just neutralised before adding buffer.

In order to obtain reliable results, it was found necessary to achieve exact neutralisation of the sample and to ensure that the compared solutions were equally well buffered.

The method fails completely in the presence of phosphate ions thus necessitating the use of the distillation procedure.

Various other methods have also been described. Fahey (66), for instance, used a "Ferron"-iron reagent. Tarun (67) again suggested the use of aluminium-eriochromecyanide with a buffer at pH 5.4. Willard and Horton (68) described a photo-fluorometric titration of fluoride ion using thorium nitrate as the titrant and quercetin as the fluorescent indicator. Up to the present, none of these methods has overcome the interference of foreign ions completely. For control assays it is best to separate the fluoride from the test sample by means of a carefully controlled distillation. The fluoride ion concentration in the distillate is then determined by a colorimetric method.

DISTILLATION .../

B.DISTILLATION METHODS.

The separation of fluoride as hydrofluosilicic acid
as generally used today was first described by Willard and
Winter (53) in 1933. Before then fluoride had been deter-
mined by precipitation (69, 70) or by volatilisation in a
perfectly dry atmosphere with silica and sulphuric acid (71,
72, 73). The methods were tedious and inaccurate. Willard
and Winter used perchloric acid and glass beads to distill
fluoride quantitatively as hydro-fluosilicic acid. The
concentration of the acid and hence the boiling point of the
mixture was maintained constant at about 135°C by gradual
addition of water through a capillary. The fluoride in the
distillate was then determined as described above under direct
methods, all interfering ions having been eliminated.

This method was later improved on by Boruff and
Abbott (56) and recently Hill and Reynolds(74) described a
further minor improvement of the process. These developments
have been incorporated in the existing standard methods (2,75)
for the determination of fluoride which are, however, still
based on the original method of Willard and Winter.

The separation of fluoride by distillation does not
eliminate all sources of error as was pointed out by Reynolds
and Hill (63). It was shown that the final titration of
fluoride is influenced by the distilling acid, the quantity of
acid used, the rate of distillation, the temperature of
distillation and incomplete retention of phosphate, pyritic
sulphur and halogens. It was found that the blank titration
of the distillate of perchloric acid alone, increased on con-
tinued distillation. On the other hand the addition of the
evaporated blank distillate to a known amount of sodium fluoride
gave rise to a slightly lowered titer.

Rickson .../

Rickson (76) studied the titration of distilled hydrofluosilicic acid with thorium nitrate and explained the reason for the low fluoride values always obtained as follows:- The fluosilicic ion hydrolyses to form silicic acid and fluoride according to the equation below.

$$Si \, F_6^{--} + 4 \, OH^- \rightleftharpoons H_2 \, Si \, O_3 + 6F^- + H_2O.$$

An acidic solution will therefore decrease the quantity of titratable fluoride, and any acid which distilles over in the fluoride separation will therefore tend to give a lower result.

By increasing the pH the formation of fluoride is more complete, but alizarin cannot be used above pH 3.5. Rickson therefore recommends the use of gallow-cyanine in a sodium acetate-acetic acid buffer.

These latter improvements are aimed at eliminating a maximum possible error of 1%. Such an error was immaterial for the purpose of the present investigations since low concentrations of residual fluoride (<1 p.p.m.) were required to be determined to the nearest first decimal only. The method prescribed by the South African Bureau of Standards (2) was thus found most suitable and reliable. This method prescribes distillation of the measured sample with perchloric acid at 135°C. The acid sample mixture first boils at little over 100°C, but the temperature rises with concentration of the acid until at 135°C, fluoride is distilled over quantitatively. In order to prevent loss of fluoride, the distillate collected prior to the boiling mixture reaching a temperature of 120°C, is returned to the boiling mixture as dilution water at a rate which maintains the boiling point at 135°C. The final distillate is then titrated with thorium nitrate to a standard pink colour of alizarin red indicator using hydroxylamine hydrochloride as buffer.

During the present investigations this method was applied as an intermittent check on routine analysis by the Stevens' method (64). Fluoride determinations were repeatedly reproducible to

0.1 p.p.m. ../

0.1 p.p.m. and recovery of added fluoride was equally
satisfactory.

11. E V A L U A T I O N   O F   D E F L U O R I D A N T S.

The efficiencies of various defluoridants can best
be evaluated in a column filter since this is the general and
most efficient method of using ion-exchange materials.   The
performance of such columns is of course dependent upon the
fluoride affinity of the exchange media when used under
specific conditions i.e. the total amount of fluoride removed
by a column is a function of the amount of fluoride which a
unit mass or volume of defluoridant can absorb.   Various other
factors such as concentration of fluoride, rate of flow, pH of
the water, and temperature, will also affect the result,   but
these can be controlled to remain constant for the purpose of
the experiment.   A measure of the defluoridising capacity
obtained in equilibrium experiments should therefore indicate
the potential value of a defluoridant when it is ultimately
used in a column.

There were several practical difficulties connected
with the use of columns (a) Many of the preparations were
powdery or gelatinous and consequently wholly unsuitable for
use in a column filter.

and   (b) a relatively large quantity of
material and elaborate testing procedure are required.

It was therefore considered that _preliminary_ testing
of a large number of preparations could best be carried out in
batch operations so as to obtain a measure of their defluori-
dising capacity while column evaluation would be reserved for
the most promising, only.   Preliminary testing involved the
following determinations:-

(a) defluoridising capacity

(b) lowest residual fluoride concentration obtainable and

(c) regeneration potentiality.

The value of (a) coupled with the value of (b) would
then be a measure of the fluoride

affinity .../

affinity of the material while the value
of (c) would indicate its practical feasibility.

Determination of (a). One gram of the defluoridant under
test was thoroughly mixed (shaking for 1 min.) with 100 ml.
of tap water which had previously been fluoridated to contain
10 p.p.m. of fluoride ion. After separation of the
defluoridant by centrifuging, the supernatent water was
decanted and the residual concentration of fluoride ion in it,
determined by Stevens' method (G4). This operation was
repeated with successive 100 ml. of fluoridised water until the
residual fluoride concentration of the supernatent liquid
exceeded 1.5 p.p.m. The total fluoride removed by 1 gram of
defluoridant was then calculated by adding together the milli-
grams of fluoride removed from each successive 100 ml. quantity
of water. Results were expressed as mg. fluoride ion per
gram defluoridant.

In some cases, 1 gram of defluoridant could not reduce the
fluoride ion concentration of even the first 100 ml. quantity of
fluoridised water sufficiently i.e. to < 1.5 p.p.m. In such
cases the quantity of fluoride removed from the 100 ml. of water
was recorded as the defluoridising capacity of the material.

Determination of (b). The lowest residual fluoride concentration
obtained in the above procedure was recorded in each case. Since,
from the quantity of defluoridant used, viz. 1 gram per 100 ml.
water, there was no question of the defluoridant becoming
saturated, the magnitude of residual fluoride gave an inverse
measure of the fluoride affinity of the defluoridant.

Determination of (c). Regeneration potentiality was measured
by the ability of fluoride saturated defluoridant to be regenerated
by admixture with a 1% solution of sodium hydroxide. The
defluoridant was submerged in the latter solution for 1 hour and
was agitated intermittently. After decanting the regenerant,
free alkali was removed by repeated water rinses. Complete
neutralisation of the defluoridant was obtained by further

washing ..../

washing with slightly acidified water.   Subsequent
defluoridising capacity was determined and recorded as a
percentage of the original capacity.   Loss of defluoridant
during regeneration indicated that regeneration would be
impracticable.

Some 55 preparations were tested by this method.
The salient features of a few representative defluoridants
are recorded in Table XI.

TABLE XI.

EFFICIENCIES OF VARIOUS DEFLUORIDANTS

Defluoridant	Defluori-dising capacity mg. F/g.	Lowest residual F^- concentration obtained (p.p.m.)	Regeneration	Physical nature
$Mg(OH)_2$	2.1	5	Impossible	Powder
$Al(OH)_3$ precipitated	2.0	2	do.	Flocculent precipitate
Al silicate complex	1.8	3	do.	Gelatinous
Silica gel	1.5	5	do.	do.
Bone meal ignited at 900°C.	0.5	5	Possible	Granular
Calcium phosphate (precipitated)	9.0	Zero	50% with loss of defluoridant	Gelatinous precipitate
Calcium phosphate (apatite) from ignition of $3Na_3PO_4 + Ca(OH)_2$ at 900°C. for 2 hours	3.5	Zero	100% no loss of defluoridant	Greenish powder
Calcium phosphate from ignition of superphosphate + lime at 900°C. for 2 hours	0.5	4	80%	do.
Activated superphosphate	2.5	0.7	100% no loss	Mixture of powder and granules

The various defluoridants which were tested may be classified as (A) Adsorbents i.e. those with adsorbent surface activity and (B) Ion exchange media. In the latter category, special attention was devoted to an exchange medium prepared from commercial superphosphate. It is therefore best dealt with separately under (C), Activated superphosphates. The defluoridants listed in table XI are discussed under these headings.

A. ADSORPTIVE DEFLUORIDANTS

A review of literature indicated that magnesium hydroxide was one of the most efficient adsorptive defluoridants: Scott et. al. (77) observed that lime-soda softening of water reduced its fluoride ion concentration. They found that this reduction was a function of the quantity of magnesium which was precipitated and concluded that fluoride was adsorbed on magnesium hydroxide. They deduced the following equation from their observations:-

$$F^- \text{ reduction } = 7\% \text{ of } [F^-] \text{ x } \sqrt{Mg \text{ removed}}$$

and established that fluoride removal by this means was uneconomical if the original magnesium content of the water was small.

Zettlemoyer (78) et. al. studied this phenomenon further and deduced that magnesium oxide is partially hydrated, followed by formation of magnesium fluoride and sodium hydroxide by metathesis. Magnesium fluoride is then adsorbed on the hydroxide forming perhaps an oxyfluoride. The average

efficiency ...../

efficiency obtained was about 13 mg F⁻ removed per gram of magnesia.

Goetz and Tiger (79) filed a patent defluoridation process based on the above principle. They suggested enriching the raw water with magnesium by mixing it with calcined dolomite.

During the present experiments, it was found that magnesium hydroxide had a limited defluoridising capacity while its failure to reduce the fluoride concentration of water to the optimum level rendered it unsuitable (refer table XI) <u>Aluminium Hydroxide</u>. The use of aluminium salts to form a floc for coagulating impurities, is common practice in water treatment and it is therefore not surprising that defluoridation by this method was investigated by several workers (80,81,82,83) The results reported indicate that the defluoridising capacity of aluminium hydroxide floc, formed from aluminium sulphate and a source of alkalinity, may vary from 5 to 10 mg.of fluoride per gram. The present studies revealed a capacity of only 2 mg/g.while the lowest residual fluoride concentration was unsatisfactory.

During the present studies (Table XI) <u>aluminium silicates</u> were prepared by mixing solutions of aluminium sulphate and sodium silicate to a resultant pH value of about 7. The washed flocculent precipitate had an average fluoride adsorption capacity of 1.8 mg. per gram. The formation of aluminium fluosilicate would enhance the capacity of the material but as will be noted from Figure II, the removal of fluoride was not in stoichiometric quantities, indicating mainly surface activity. The capacity dropped off with lowering of fluoride ion concentration of the water and below 3 p.p.m. of fluoride no further reduction could be obtained.

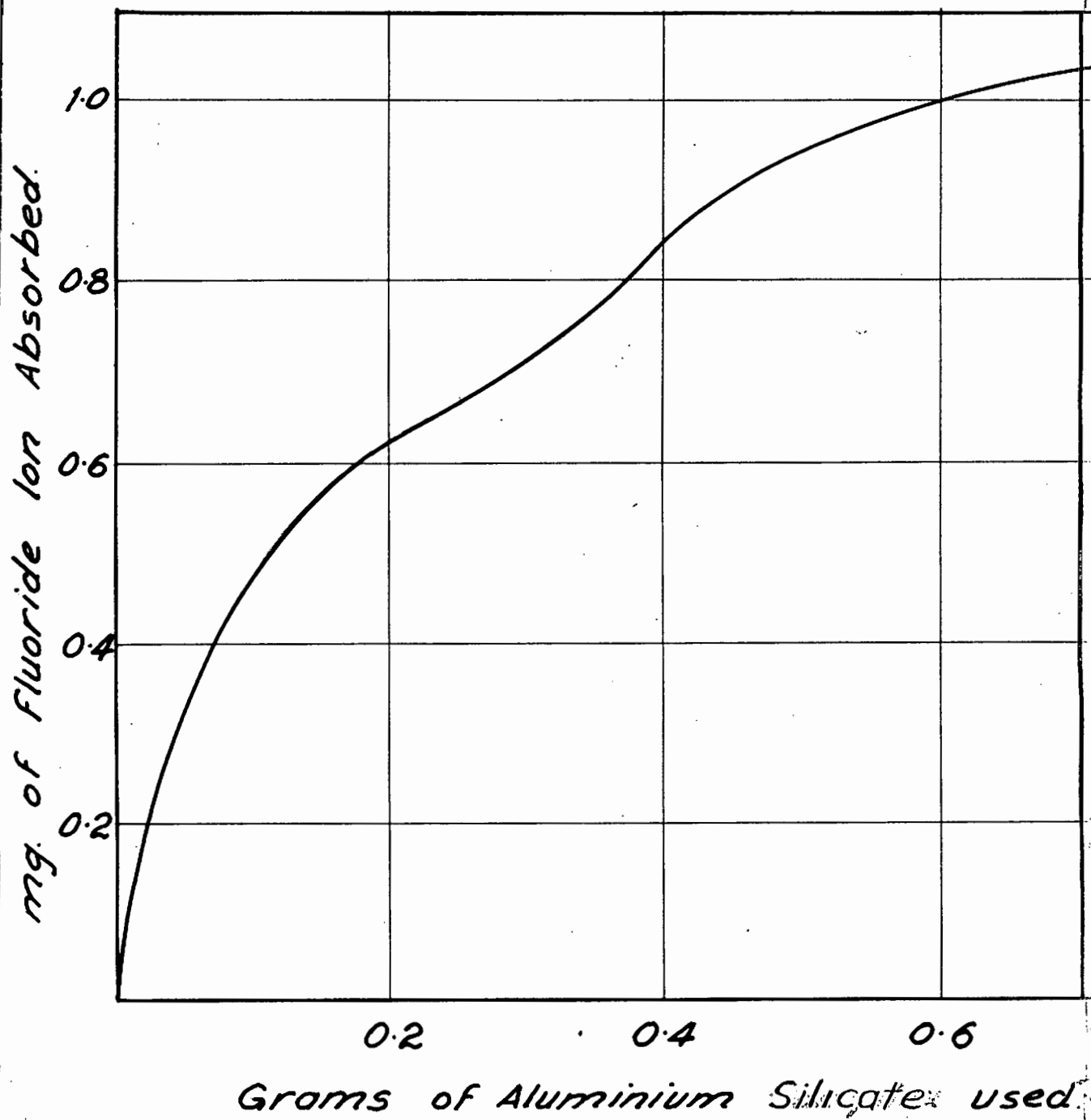Both aluminium hydroxide and aluminium silicates were thus found unattractive defluoridants.

Figure II
Defluoridative Capacity of Aluminium.

Silica gel was prepared by slow acidification of 10% sodium silicate solution. The product could not remove fluoride from water which contained less than 5 p.p.m. of fluoride ion.

Activated carbon (84) requires preliminary acidification of the fluoride bearing water to a pH value of 3. Such excessive acidification and subsequent neutralisation render the process impracticable in consequence of which this method was not investigated.

As is evident from Table XI as well as the previous discussion the adsorptive defluoridants all had comparatively low affinities for fluoride. In addition their gelatinous consistency rendered them unsuitable for use in a filter column and finally their inability to be regenerated successfully led to the decision to suspend their investigation in favour of ion exchange defluoridants.

B. ION EXCHANGE DEFLUORIDANTS.

Commercial anion exchange resins remove fluoride together with all other anions present in a water. Such complete demineralisation is, however, not required for domestic use and the high cost is thus not warranted, particularly in view of the fact that fluoride bearing waters are generally highly mineralised. It appeared, therefore, that economical defluoridation by ion exchange requires media which have a high selectivity for fluoride ions.

Defluoridation with bone meal and other phosphatic materials had previously been studied by other workers (85→91) They attained various degrees of success but apparently did not realise that they were in fact using a selective ion exchange material. In any case, this is not mentioned except by Smith (85) who suggested that the fluoride absorption of bone was accompanied by formation of fluorapatite. No further attempt was made, however, to investigate the implications of ion

exchange .../

exchange by apatite.   The present studies indicated that apatite formation was of primary importance for efficient defluoridation and detailed investigations, as are described in the following pages, were undertaken in attempting to develop suitable materials.

B,1. Bone Meal was ignited at 900°C and thereafter soaked in 1% sodium hydroxide solution for 24 hours.   Samples not ignited previously, were soaked in 1% and 5% solutions respectively.   The defluoridising capacities of these preparations were small (Table X1) and became negligible when the fluoride concentration of a water was near the optimum limit.   Its possible use was thence ignored.

B,2. Precipitated Phosphates:

The principal chemical constituent of bone, tricalcium phosphate, was prepared synthetically and used as a defluoridant by Elvove (86), Adler et al (87) and others (88, 89, 90).   Van der Merwe (9ɪ) recommended the use of freshly precipitated tricalcium phosphate prepared from a solution of superphosphate of lime and milk of lime.

None of these recommendations have as yet found any practical application, primarily on account of their high cost and cumbersome procedure.

The results of initial trials with precipitated calcium phosphate (refer Table XI) were nevertheless so promising that further detailed studies ensued.

The results of defluoridation tests with various phosphates which were prepared in the laboratory are recorded in Table XII.   Except where otherwise indicated, all preparations were precipitated in aqueous medium by mixing 10% solutions or suspensions of the reagents in the recorded order.   All precipitates were washed free of electrolytes before they were tested.   Crystal structure was determined by means of X-ray diffraction, in order to indicate the presence or absence of hydroxy apatite.

No.	Preparation	Physical Properties	Analysis % by weight			Defluoridising capacity mg.F / gram	Lowest residual F concentration obtained p.p.m.	Ability to be regenerated with NaOH soln.	Remarks
			$^{++}$ Ca	$^{---}$ PO4	Ca/ PO4 ratio				
1	Tricalcium phosphate (B.D.H. Reagent)	Precipitated powder	-	-	-	1.1	7.1	Partially	-
2	$2\ Ca_3(PO_4)_2$ reagent + $CaCl_2$ + 4 NaOH	Colloidal precipitate				1.1	4.4	Partially soluble	Unsuitable on account of colloidal nature.
5	KH_2PO_4 + 0.7 Na silicate + 0.6 $CaCl_2$ + 0.15 $Al_2(SO_4)_3$	Gelatinous acidic				2.1	5.4	Impossible	Drying destroyed
7	KH_2PO_4 + 0.7 Na silicate + 1.5 $CaCl_2$ + 0.15 $Al_2(SO_4)_3$ + 0.9 Ca(OH)$_2$	Gelatinous alkaline				3.8	2.8	Impossible	activity
8	0.7 Na silicate + (KH_2PO_4 + 1.5 $CaCl_2$ mixture) + 0.5 Ca(OH)$_2$	Gelatinous alkaline				5.2	1.0	Impossible	completely
9	6 KH_2PO_4 + 10 Ca(OH)$_2$	Granular and brittle, alkaline				2.4	0.2	Partially soluble	-
9a	6 KH_2PO_4 + 10 Ca(OH)$_2$ Dried at 160°C	Amorphous powder				2.1	1.4	-	-
10a	2 KH_2PO_4 + 3 $CaCl_2$ + 4 NaOH	Gelatinous precipitate	41.3	44.0	.94	4.6	0.2	Partially soluble	Low recovery
15	2 KH_2PO_4 + 3 $CaCl_2$ + 2 NaOH	Granular acidic	26.3	59.4	.442	Nil (PO4 dissolves in water)		Partially soluble	-
12	3 Ca(OH)$_2$ + 2 H_3PO_4 conc. solution 114%	Granular alkaline	-	-	-	3.7	2.6	Partially soluble	Reaction slow and incomplete.
12a	No.12 Dried at 160°C	Amorphous powder	-	-	-	2.6	3.2	-	-
13	3 $CaCl_2$ + 2 H_3PO_4 + 6 NaOH	Gelatinous precipitate	40.3	51.3	.786	3.4	0.2	Partially soluble	Unsuitable on account of colloidal nature

DEFLUORIDISING PROPERTIES OF PRECIPITATED PHOSPHATES

No.	Preparation	Physical Properties	Analysis % by weight			Defluoridising capacity mg.F / gram.	Lowest residual F concentration obtained p.p.m.	Ability to be regenerated with NaOH soln.	Remarks
			Ca^{++}	PO_4	Ca/PO_4 ratio				
14	$4\ CaCl_2 + 2\ H_3PO_4 + 8\ NaOH$	Alkaline micro-apatite	39.3	53.8	.721	9.0	zero	Original activity cannot be restored	-
14a	No.14 Dried at $110^{\circ}C$	Apatite	-	-	-	3.9	0.5		
14b	No.14 Ignited at $900^{\circ}C$	Well defined apatite	-	-	-	0.5	8.8	-	Ignition destroyed activity.
10b	$2\ Na_3PO_4 + 3\ CaCl_2$	Granular	34.6	57.5	0.602	1.8	5.6	Partially destroyed	-
10c	$2\ Na_3PO_4 + 3\ CaCl_2 + 1\ NaOH$	Gelatinous micro-apatite	37.0	48.8	0.758	5.1	0.3	Partially dissolved	-
10d	$2\ Na_3PO_4 + 1\ NaOH + 4\ CaCl_2$	Well defined apatite	-	-	-	4.5	0.6	Partially dissolved	-
11a	$3\ CaCl_2 + 2\ Na_3PO_4\ \&\ 1\ NaOH$	Well defined apatite	-	-	-	5.4	0.4	Partially dissolved	Efficient
11b	$(3\ CaCl_2 + 1\ NaOH\ mixed) + 2\ Na_3PO_4$	Amorphous mixture	-	-	-	5.3	0.4	Partially dissolved	mixing
11c	$3\ CaCl_2 + (NaOH + 2\ Na_3PO_4\ mixed)$	Amorphous mixture and micro-apatite	-	-	-	6.1	zero	Partially dissolved	ensured by
11d	$4\ CaCl_2 + 2\ Na_3PO_4 + 2\ NaOH$	Well defined apatite	37.3	48.3	0.773	4.5	0.4	Partially dissolved	continuous
11e	$4\ CaCl_2 + (2\ Na_3PO_4 + 2\ NaOH\ mixed)$	Amorphous mixture and micro-apatite	37.2	48.2	0.773	6.5	zero	Partially dissolved	air blast
25a	$3\ Ca(H_2PO_4)_2$ solution of superphosphate $+ 6.6\ Ca(OH)_2$	-	32.1	41.3	0.777	2.0	0.5	Partially dissolved	-
25d	$3\ Ca(H_2PO_4)2$ solution of superphosphate $+ 5.6\ Ca(OH)_2 + 0.6\ NaOH$	-	-	-	-	3.1	0.9	Partially dissolved	-
25e	No.25a Ignited at $900^{\circ}C$	Very hard greenish lumps—apatite	-	-	-	0.04	8.5	-	-

OBSERVATIONS: The attempts to imbed phosphate on silicate com-
plexes by mutual precipitation did not produce efficient
defluoridants. Especially the introduction of aluminium
seemed to reduce the capacity (see preparations 5, 7 and 8).

Tricalcium phosphate reagent had only limited de-
fluoridising capacity (refer preparation 1 and 2), but fresh-
ly precipitated phosphates showed much higher affinities
(refer preparations 9 to 14). The original combination of
the reacting ions used to form the precipitate did not affect
the resulting product materially provided that their ratio was
such that formation of hydroxy apatite was possible.

Best efficiencies were obtained when the media were
precipitated in decidedly alkaline solution with a pH value
above 12. Under these conditions a microcrystalline apatite
structure and a high Ca/PO_4 ratio was obtained. Excess calcium
reagent and/or high alkalinity produced a colloidal precipitate
which could not be used satisfactorily. These results indi-
cated that high defluoridising capacities were obtained only
when the precipitate contained microcrystalline apatite.

Hodge et al (92) reported that the mode of mixing the
reagents determined the crystalline structure of the precipitated
calcium phosphate. Experimentally, however, the variation in
defluoridising capacity of such preparations was insignificant
(refer preparations 11a, b, c, d and e).

The capacity of the material prepared from super-
phosphate solution was relatively low (refer preparation 25 a
and d).

The average defluoridising capacity of the precipitates
(10 to 14) compared favourably with that reported by Elvove and
others, viz 5.3 mg/gram as against 3.7 mg/grm. This was
probably due to additional fluoride adsorption on the gelatinous
precipitates. All the preparations were, however, unsuitable
for practical application due to -

(a) ..../

(a) the soft powdery nature of the precipitates

(b) the loss of activity upon drying or ignition, and

(c) inability to be regenerated after saturation with fluoride.

<u>Regeneration</u>:

Extensive regeneration tests were carried out with two preparations which were selected because of their high defluoridising capacity. A suspension containing 0.5 grams of freshly precipitated defluoridant was repeatedly saturated with fluoride and thereafter regenerated. Several regenerants were used as indicated in Table XIII. Fluoride and phosphate contained in the spent regenerant and washings were determined in each case.

Regeneration of the defluoridants resulted in such severe loss of efficiency that it rendered the process impracticable even under the most favourable conditions. The reduction in capacity was in direct relation to the percentage of fluoride recovered during regeneration. The dissolution of phosphate in the regenerant caused a considerable loss of material and indicated that a more stable structure was required if the material were to be regenerated successfully. It was considered that drying or ignition of the gelatinous phosphatic precipitates would achieve this, but the experiments recorded in table XII showed that drying attenuated their efficiency.

Conclusions: The inherent deficiencies of precipitated tricalcium phosphates (Refer observations a, b and c of this sub-section) are perhaps the main reason for the lack of application of the recommendations of previous workers in this field (86→91). As illustrated in table XII, most efficient defluoridation was obtained when the precipitates contained micro-crystalline hydroxy apatite. Since well-defined apatite crystals are insoluble in dilute alkalis, it was thought that a defluoridant which consisted of such crystals only, would be free from the above deficiencies. A careful review of literature and especially the publication of Beevers and McIntire (52), confirmed that pure apatites should be suitable exchange media for defluoridation.

The latter workers studied the crystal structure of natural apatites occuring in various rock formations and concluded that in hydroxy apatite, calcium, phosphorus and oxygen atoms were arranged to form hexagonal tubes along the C-axis of the crystal while hydroxide ions fitted neatly inside these tubes. The particular linkage of calcium phosphorus and oxygen atoms afforded a very rigid structure whereas the hydroxide ions was somewhat loosely bound. Hence, the hydroxide ions could be replaced, but only by ions of similar weight, charge and effective radius. Thus, introduction of fluoride ions which are very slightly smaller than hydroxide ions, causes a slight contraction of the structure which

facilitates..../

facilitates the exchange.

In view of these considerations, further work was undertaken on the production of stable apatites.

B,3. Ignited Phosphates

In order to produce a stable apatite, i.e. one which could be regenerated efficiently, various stoichiometric dry mixtures calculated to produce hydroxy or fluorapatite were ignited at 900°C for 2 hours.   The ignited material was ground and then washed and tested as before.   The results are recorded in Table XlV.

TABLE X1V

DEFLUORIDISING PROPERTIES OF IGNITED PHOSPHATES

| No.	Preparation	Physical Properties	Defluoridising capacity mgF^-/gram	Lowest residual F^- concentration obtained p.p.m.	Ability to be regenerated with NaOH solution.	Remarks
21a	$3Ca_3(PO_4)_2 + CaF_2 \longrightarrow 2CaFCa_4(PO_4)_3$	Soft powder apatite	Nil	(Could not be washed free of fluoride)		Reaction incomplete
21b	$3Na_3(PO_4) + 5CaF_2 \longrightarrow CaFCa_4(PO_4)_3 + 9NaF$	Fused mass: no definite crystal structure	Nil	(Could not be washed free of fluoride)		Reaction incomplete
21c	$3Na_3(PO_4) + 4Ca(OH)_2 + CaF_2 \longrightarrow CaFCa_4(PO_4)_3 + 8NaOH + NaF$	Fused mass: no definite crystal structure	0.4	5.2	-	No regeneration attempted on account of low affinity
21d	$3Na_3PO_4 + 5Ca(OH)_2 \longrightarrow CaOHCa_4(PO_4)_3 + 9NaOH$	Soft greenish powder micro crystalline apatite	3.5	zero	Regenerate 6X without loss	Excess causticity neutralised with HCl.
24	$(3Ca(H_2PO_4)_2 + 6CaSO_4 + CaF_2) + 7Ca(OH)_2$ (Main ingredients of "Super") $\longrightarrow$ apatite + solubles	Soft greenish powder apatite	0.5	4	Possible	Difficult to wash free of SO_4^{--} and F^-
31	"Super" + $7Na_2CO_3 \longrightarrow$ Apatite + solubles	Apatite powder	0.1	3	Possible	Reaction incomplete
34	"Super" + $7Na_2CO_3 + Ca(OH)_2 \longrightarrow$ Apatite + solubles	Yellowish powder	0.2	4	Possible	Reaction incomplete
33	"Super" + $3.5 Na_2CO_3 + 3.5 Ca(OH)_2 \longrightarrow$ Apatite + solubles	Apatite powder	Nil	-	Possible	Could not be washed free of SO_4^{--}
32	"Super" + $14NaOH \longrightarrow$ Apatite+solubles	Fused mass apatite	0.1	4	Possible	-

Note: "Super" means commercial superphosphate of lime.

The use of superphosphate as source of raw material was attempted since it is available at reasonable cost in South Africa. None of these preparations, however, were satisfactory defluoridants although they all contained apatite. In most cases incomplete interaction of the ingredients occurred with the resultant powder losing phosphate during washing and defluoridation. Whenever complete fusion of the ingredients occurred, the product was unsuitable on account of its non-porous large crystalline structure (refer 21b and c and 32). Only one of the preparations, 21d, which consisted of partially disintegrated apatite had efficient defluoridising properties. Ion exchange is obviously only effected on the surface of apatite crystals. Micro crystals are therefore essential for efficient defluoridation.

Preparation 21d could be regenerated without loss of efficiency but unfortunately its fine consistency prevented its use in a conventional filter. Various attempts to imbed it on carriers were unsuccessful. Production costs were also very high.

C. ACTIVATED SUPERPHOSPHATE DEFLUORIDANTS.

Previous experimental data indicated clearly that an apatite of microcrystalline structure was most efficient in exchanging fluoride and hydroxide ions as illustrated by the following equation:-

$$CaOH.Ca_4(PO_4)_3 + F^- \rightleftharpoons CaF.Ca_4(PO_4)_3 + OH^-$$
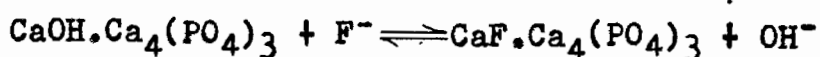
Since superphosphate contains partially decomposed fluorapatite, it was considered a possible raw material for the production of microcrystalline apatite via direct neutralisation of its acidity. Such a synthetic preparation would probably be a fluorapatite, on account of its derivation, and hence it would have no further fluoride absorbing properties. If, however, excess alkalinity is used for the neutralisation, it may be

expected .../

expected that at least part of the fluoride ions in the apatite
structure will be replaced by hydroxide ions i.e. the above
reaction will be from right to left.

The feasibility of this hypothesis was borne out
by subsequent experiments, while the relatively low cost of
superphosphate in South Africa, enhanced the attraction of its
direct utilisation as a defluoridant.

C,1. Preparation:

Activated superphosphate was prepared by soaking
superphosphate of 19% P_2O_5 in a solution of sodium hydroxide
for 24 hours with intermittent agitation.   Various concentrations
of sodium hydroxide were used - always providing sufficient for
both neutralisation and excess causticity.   About 0.32 grams
sodium hydroxide was used per gram of superphosphate.   After
decantation of the supernatent liquor the solid material was
washed free of alkali and tested as described before.   Ground
raw phosphate rock, as well as a mixture of "super" and raw
phosphate, were treated similarly for purpose of comparison.

C,2. Performance:

The results of tests carried out are recorded in Table XV.

Best results were obtained when a 5% solution of sodium
hydroxide was used (refer No. 35).   Such a concentration also
provided a convenient volume of liquid (6 ml./g.) for immersion
of the solid material and ensured excess causticity equivalent
to 1% sodium hydroxide.   For efficient activation it was
essential to neutralise all acidity of the superphosphate by
providing sufficient time of reaction and adequate agitation of
the mixture.   When these requirements were not complied with, a
product was obtained which was partially soluble and inactive as
a defluoridant.

The defluoridising capacity of the preparations was
not as high as that of some of the precipitated phosphates (refer
Table XI) but their ability to be regenerated together with the

simplicity ..../

No.		bility to be regene- rated with NaOH Soln.	Remarks
	Raw St	—	—
23	"Super solut	egenerated times with- ut loss.	Inefficiency due to alkalinity not being neutralised
35	"Sup solu	egenerated X without- oss	Activation caused 32.5% loss in weight.
36	"Sup solu	egenerated X without loss.	37.5% loss in weight.
37	"Sup solu	egenerated X without loss.	27.6% loss in weight.
41	Phos NaOH	Possible	Could not be washed free of soluble fluoride.
42	Supe (3:2 NaOH	Possible	Neutralisation very slow - about 5 days.

simplicity and possible low cost of manufacture was most attractive.

It will be observed that treatment with sodium hydroxide converted superphosphate back to an apatite. Although phosphate rock from which "super" is manufactured contains fluorapatite, the former could not be used for the preparation of defluoridants by the present method (refer No. 41). It would seem that the initial degradation of the apatite structure caused by acid treatment is an essential preliminary to the production of a defluoridant. A mixture of "super" and raw phosphate could similarly not be activated to the same capacity as pure superphosphate (refer No. 42).

A comparison of the analysis of superphosphate before and after treatment showed that most of its sulphate content was removed while the ratio of calcium to phosphate was increased from 0.69 to 0.76 due to initial solubility of phosphate, thus favouring the formation of apatite. The average overall loss in weight amounted to one third of the original weight of "super" used.

Analysis of the activated phosphate indicated that only a small portion of the fluoride present in superphosphate had been removed by the treatment. Apparently fluoride ions inside the tubular structure (52) of the apatite crystal could not be replaced with hydroxide ions. Thus ion-exchange is presumably only effected at the ends of these "tubes" i.e. on the surface of the crystal. It is obvious therefore, that a micro-crystalline structure is required for maximum exchange capacity. X-ray diffraction studies of the activated superphosphate indicated such a micro-crystalline apatite structure, almost similar to precipitated apatites.

C.3. Significance of pH:

For efficient defluoridation it was found necessary to maintain the pH value of the medium and water to be defluoridated,
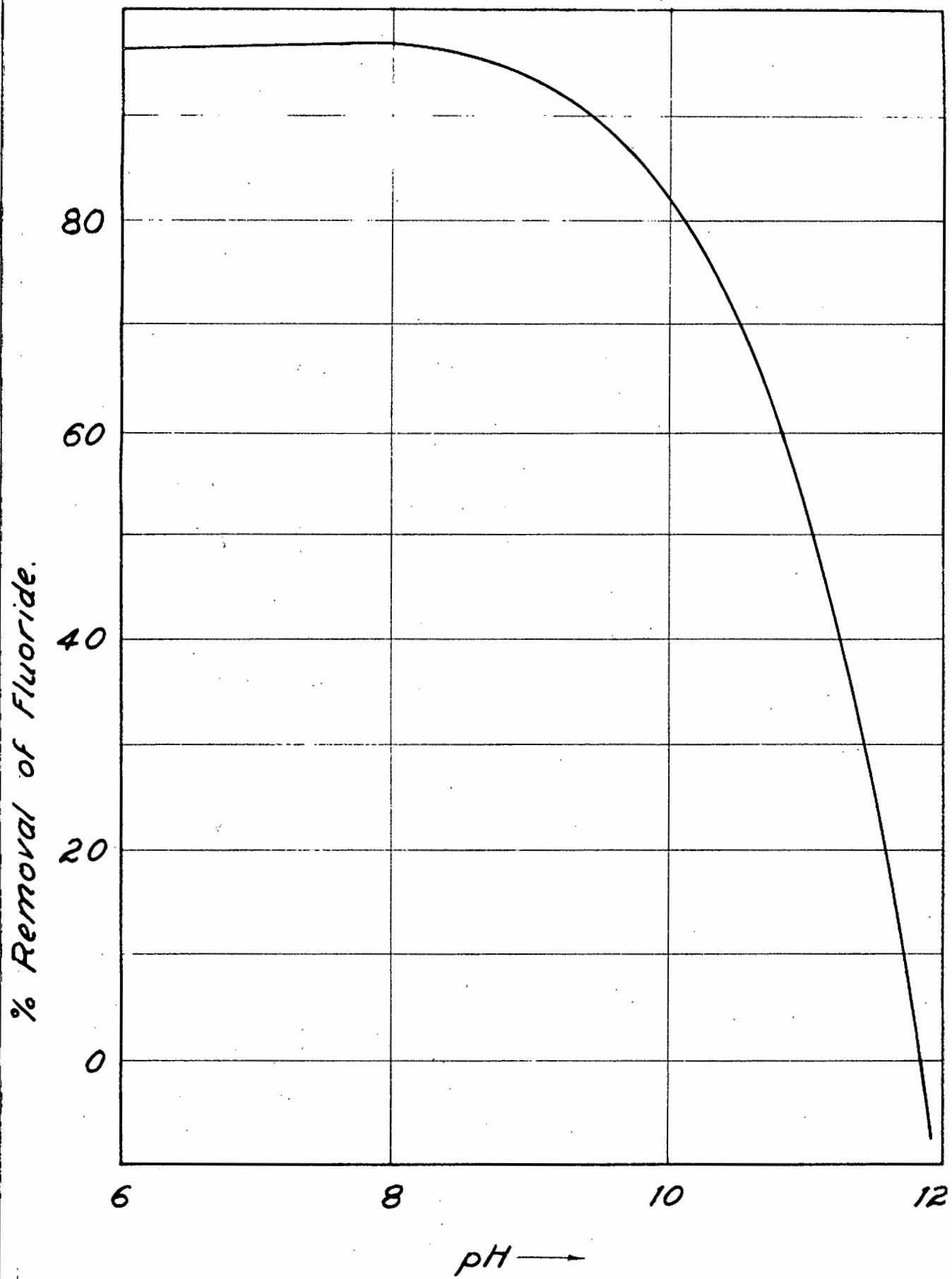
between ..../

Fig. 12.

Effect of pH on Fluoride Removal.

between 6 and 8.   Below pH 5.5, phosphate was partially
dissolved and above pH 8 the efficiency dropped rapidly as
illustrated in Figure 12.

This relationship between fluoride and hydroxide
concentration of a water in contact with a defluoridant is
demonstrated if the law of mass action is applied to the
reaction.

$$CaOH.Ca_4(PO_4)_3 + F^- \rightleftharpoons CaF.Ca_4(PO_4)_3 + OH^-$$
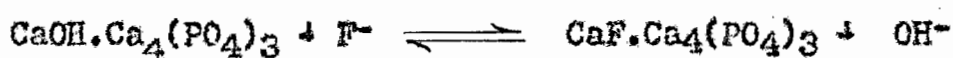
An ion-exchange of this type is essentially
crystalline and the apatite crystal is therefore not subject
to the swelling effect normally encountered with resinous ion
exchange materials.   Consequently, while both hydroxy and
fluorapatite are present in solid phase, the mass-action
equation may be approximately used in the simple form:-

$$[F^-] = K[OH^-]$$

It follows that at high pH values the reaction would
proceed to the left, i.e. fluoride in the apatite will be
replaced by hydroxide and pass into solution as ions. Similarly
low pH values will favour defluoridation, i.e. fluoride ions
passing into solid phase. The particular structure of apatite
(52) favours absorption of fluoride rather than hydroxide ions
because of the former's smaller effective radius. Consequently
a large excess of hydroxide ions is required to displace the
equilibrium in the direction of regeneration.

On the other hand it would follow that defluoridation
should proceed at relatively high pH values.   This does, in
fact, occur but the extremely low concentration of fluoride ion
required in a defluoridated water necessitates a liberal
reduction of pH value.

It was found experimentally that the fluoride ion
concentration of a water could not be reduced to the optimum
value of 1 p.p.m. if the pH value of the medium was above 8.5
while at pH values above 12 regeneration of apatite occurred
rapidly.

3.

111. ACTIVATED SUPERPHOSPHATE
FILTERS.

The treatment of a water supply is most conveniently performed by passage through a conventional filter with a granular bed. The activated superphosphate used during initial experiments was a mixture of powder and granules such as is normally sold. When superphosphate was graded by careful screening the various fractions responded equally well to activation. It was thus possible to prepare defluoridant granules, suitable for use in an ion exchange filter.

A. PREPARATION OF THE FILTER MEDIUM.

Superphosphate (19% P_2O_5) granules of -20, + 48 mesh, were found most suitable for use in a column filter. Such granules were agitated intermittently with excess sodium hydroxide solution (6 ml. of 5% NaOH per gram of superphosphate) for about 24 hours. Fine particles of phosphate resulting from attrition during agitation were decanted with the spent sodium hydroxide solution. The granules were then washed repeatedly with tap water to a pH value of 10— sulphate and any soluble phosphate being washed out simultaneously. About 10 washings were required and the turbidity which occurred was decanted with the washings.

This method of preparation resulted in a gross loss in weight of 40%. The bulk density of the prepared granules was 0.55 grams per ml. The granules were hard and porous and ready for use.

The behaviour of this defluoridant was investigated in a laboratory filter column, as a preliminary to pilot plant studies.

B. LABORATORY FILTER STUDIES.

A filter bed of 2 cm. diameter by 20 cm. deep was used to defluoridise water containing 10 p.p.m. of fluoride ion.

Twenty-eight grams of defluoridant granules were used in the filter (Figure 13).
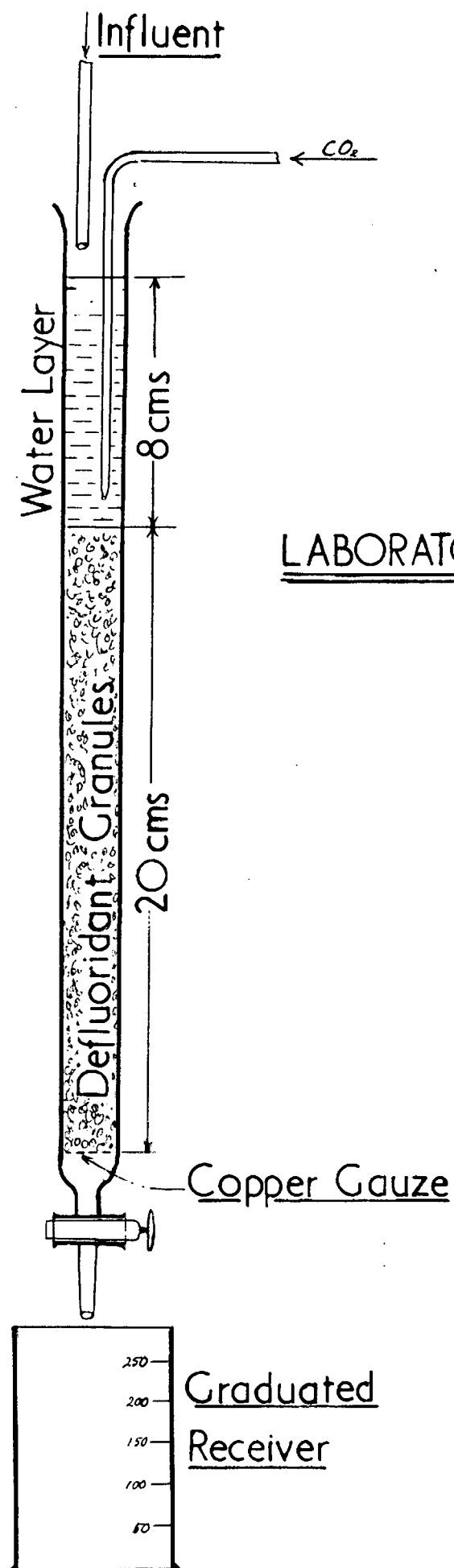

FIGURE 13

LABORATORY DEFLUORIDATOR

B.1. <u>Defluoridation</u>: In order to maintain the pH value of the
bed at an optimum value (about 7) the influent to the filter
was acidified to a pH value of 6, via the introduction of
carbon dioxide (refer "Acidification of Feed Water" Item III,
C, 2 of this Chapter.)

Measurements of rate of flow and quality of effluent
was taken at regular intervals.   Table XVI gives the results
of such measurements in a typical cycle.

<u>TABLE XVI</u>

DEFLUORIDATION WITH LABORATORY FILTER

Number of litres passed through when tested	Rate of flow Mins/ 250 ml.	Residual F^- in p.p.m.	pH	SO_4^{--} p.p.m.	PO_4^{---} p.p.m.	REMARKS
1	9	1.5	9.1	200	Nil	
3	5	0.5	7.1	180	20	Initial solubility of PO_4^{---} probably due to incomplete neutralisation
6	5	0.9	7.0	140	20	
8	18	1.1	7.0	110	Nil	Controlled rate of flow.
8½	4	1.2	7.1	–	–	Maximum rate of flow
10	12	1.3	7.1	70	Nil	Defluoridant becoming saturated with fluoride
11	9	1.6	6.8	60	Nil	
12	11	2.0	6.7	60	Nil	

A composite sample of effluent had a fluoride ion
concentration of 1.2 p.p.m. which meant that the filter had
a defluoridising break-through capacity of 3.5 mg. F^-/g. of
defluoridant.   The defluoridated water was palatable and had
no foreign taste or odour.   Variation of flow rate through
the filter did not affect the efficiency of defluoridation.
The maximum rate obtained with the particular granules used

was ..../

was 60 ml./min. The residual fluoride ion concentration
in the effluent decreased during the initial stage of the
run as a result of the decrease in its pH value. Thereafter
it increased gradually from 0.5 to 2 p.p.m. due to saturation
of the media. When the latter value was reached, the filter
was regenerated.

It was found that sulphate was dissolved in the
filtrate during the first two or three cycles of using a
freshly prepared defluoridant. Complete removal of sulphate
could be obtained by exhaustive washing during the preparation
of the defluoridant but this would be unnecessary since the
slight increase in sulphate concentration would not affect
the potability of the water. The dissolution of phosphate
could be overcome by adequate neutralisation of all acidity
in the superphosphate granules.

B,2. Regeneration:

After the material had been saturated with fluoride
ion, it was regenerated in the filter by upward displacement
with a 1% solution of sodium hydroxide followed by a water
rinse. It was found that 8 ml. of solution per gram of
material was sufficient to raise the pH value of the filter
bed to 12, at which value fluoride is exchanged for hydroxide.
(Refer figure 12).

The quantity of wash water required to remove
excessive alkalinity was also about 8 ml. per gram of material.
It was not necessary to use defluoridated water for this purpose
because the pH was not reduced sufficiently to allow for
exchange of fluoride. (Refer figure 12). Although complete
neutralisation of the filter bed was not attained by this degree
of washing, defluoridation of influent (adjusted to pH value
below 6 with CO_2 gas) commenced as soon as the pH of the effluent
dropped below 9. The defluoridation cycle could thus be
started while gradual neutralisation of the filter bed was
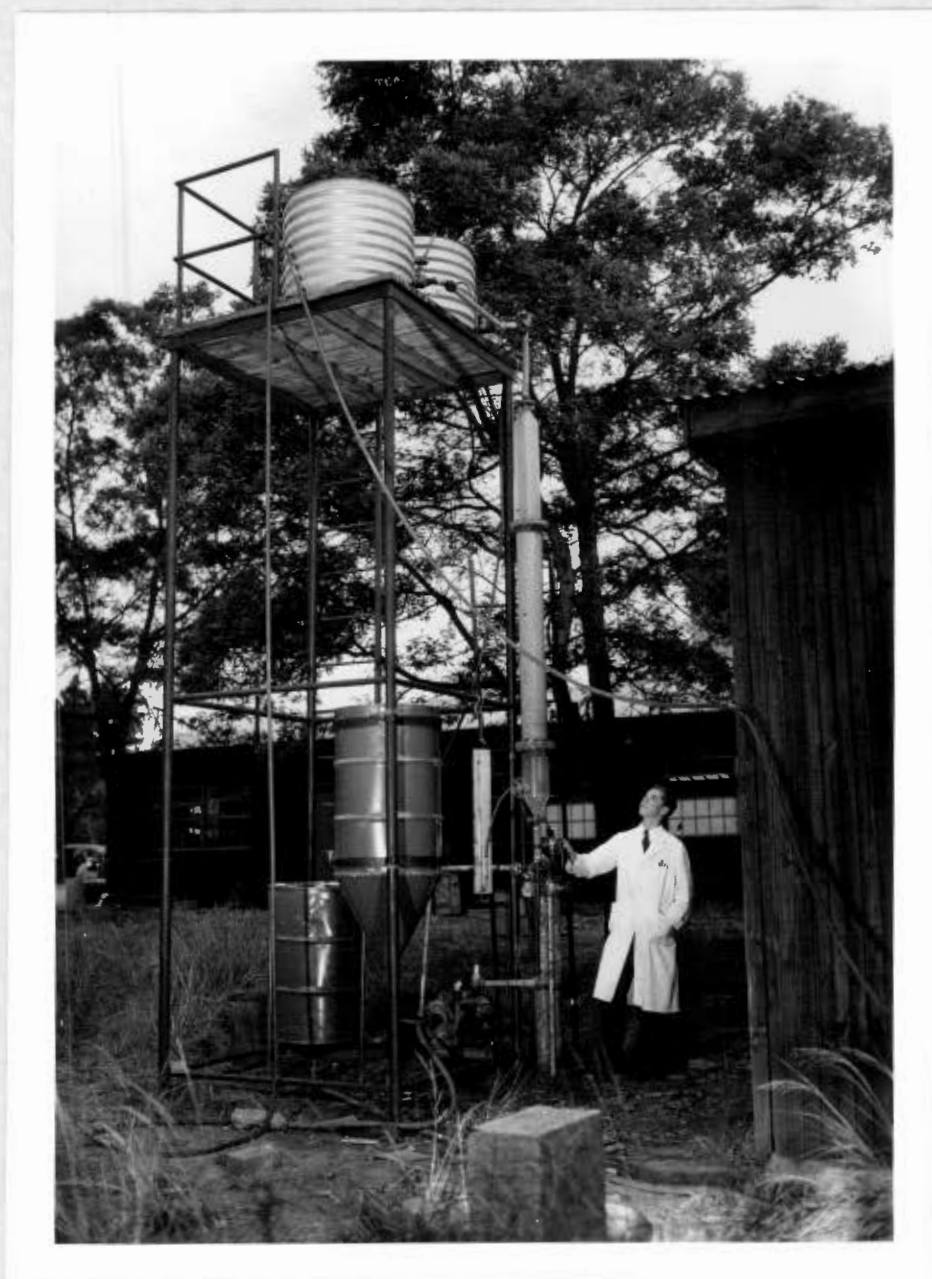effected. A considerable saving in wash water resulted from
this procedure.

C. .../

FIGURE 14

DEFLUORIDATION PILOT PLANT.

C. PILOT PLANT STUDIES.

Activated superphosphate granules (28 lb.: -10 + 48 mesh) were introduced into a filter column (5¾" internal diameter, 7'4" long). The filter shell consisted of ¼" thick "perspex" and the 54" deep bed of defluoridant was retained on a "perspex" plate perforated with 1/16" holes. The apparatus (Fig. 14) provided for introduction of carbon dioxide, i.e. acidification of the feed water, as well as for backwashing the filter during regeneration.

C. (1. Defluoridation

Feed water containing varying concentrations up to 100 p.p.m. of fluoride ion was first acidified to a pH value of approximately 6 in two 50-gallon tanks which were used alternately. Defluoridation was accomplished by gravitational filtration through the column. Average samples of influent and effluent for each successive batch of 40 gallons were analysed. Table XVII contains data relative to the fourth defluoridation cycle. These data are typical of the results obtained throughout the tests.

TABLE XVII

DEFLUORIDATION WITH A PILOT SCALE FILTER COLUMN

No. of batch (40 gal)	Rate of filtration min/40 gal	Influent F⁻ Conc. (p.p.m.)	pH	Effluent F⁻ Conc. (p.p.m.)	pH	SO₄⁻⁻	Remarks
1	70	45	5.8	2.6	8.9	No increase	High pH caused inefficient defluoridation
2	80	46	5.7	0.24	7.1	do	Controlled rate of flow
3	60	42	5.7	0.24	7.0	do	Maximum gravity flow
4	70	70	6.0	0.6	7.2	do	
5	100	100	6.0	0.75	7.2	do	
6	90	90	5.9	1.1	7.3	do	

Average .../

TABLE XVII (Contd.)

;Average fluoride ion concentration of influent = 65.5 p.p.m.

;Average fluoride ion concentration of effluent = 0.9 p.p.m.

;Total fluoride ion removed from water = 0.155 lb.

;i.e. 0.0055 lb. F⁻/lb. of defluoridant or 5.5 mg./g. or

;0.19 lb./c.ft.

Observations

(a)   The performance of this filter was in accordance with the observations made on the laboratory filter.

(b)   Fluoride ion concentration of the influent did not affect the efficiency of the defluoridant.

(c)   At the start of a defluoridation cycle fluoride ion concentration of the effluent was relatively high (2.6 p.p.m. and higher) since at the high pH value (8.9) the removal of fluoride from solution is incomplete. The high pH value was due to adsorbed alkalinity of the bed, an important factor to consider in acidifying the influent.

(d)   During the major part of the cycle defluoridation to less than 1 p.p.m. of fluoride ion was attained.

(e)   Repeated use of the defluoridant removed all soluble phosphate and sulphate. From the fourth cycle onwards no increased concentration of these ions could be detected in the effluent. A slight increase of bicarbonate concentration persisted due to introduction of sodium hydroxide during regeneration and carbon dioxide during defluoridation.

(f)   The rate of flow through the filter varied according to the condition of fine particles on the upper surface of the filter. It was found to be from 20 to 40 gallons per hour. Variation of the flow rate did not affect the efficiency of the defluoridation process.

C.2. Acidification of Feed Water

The exchange reaction of apatite with fluoride and hydroxyl ions, viz.

$$CaOH.Ca_4(PO_4)_3 + F^- \rightleftharpoons CaF.Ca_4(PO_4)_3 + OH^-$$
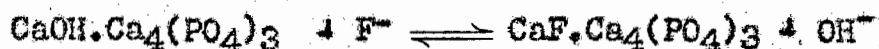
requires a low pH value for complete removal of fluoride ions from solution. Alkaline natural waters therefore require acidification to a pH value of about 7. In order to maintain an optimum pH value during exchange it is further necessary to provide "reserve acidity", undissociated acid, for neutralisation of adsorbed alkalinity on the defluoridant as well as of hydroxyl ions which are liberated. The acid required for the latter purpose would be proportional.to the fluoride content of the influent while adsorbed hydroxide would be neutralised or converted to bicarbonate during the initial stages of a defluoridation cycle.

In order to assess the most practical method of providing these acid requirements, influent was acidified with some common acids and carbon dioxide as indicated in Table XVIII. Untreated water had a pH value of 8.3 and acid additions were limited so as not to reduce the pH value to less than 5.5 since apatite tends to dissolve at lower pH values. Figure 15 depicts pH reductions obtained by bubbling carbon dioxide through tap water.

Table XVIII   Efficiency of Various Acidifying Agents

| Acid	Quantity added to 40 gal. feed water		Final pH of feed water	Percentage fluoride removed by defluoridation of feed water with		Remarks
	Weight in grams	Gram equivalents of acid		10 p.p.m. of $[F^-]$	100 p.p.m. of $[F^-]$	
Acetic	10.5	0.175	5.6	90 i.e. <1 p.p.m. in effluent	50	Filter blocked easily
Hydro-chloric	5.5	0.151	5.5	95	40	When defluoridising 100 p.p.m. pH value of effluent rose to 10 with consequent inefficiency
Sulphuric	8.1	0.165	5.6	97	–	
$NaHSO_4$	35	0.292	5.9	96	50	Additional buffer capacity provided by larger concentration of acid equivalents
Carbon dioxide	260	–	5.9	100	100	)Acid equivalents cannot)be calculated because of)incomplete solution of)gas
do.	220	–	6.0	100	100	
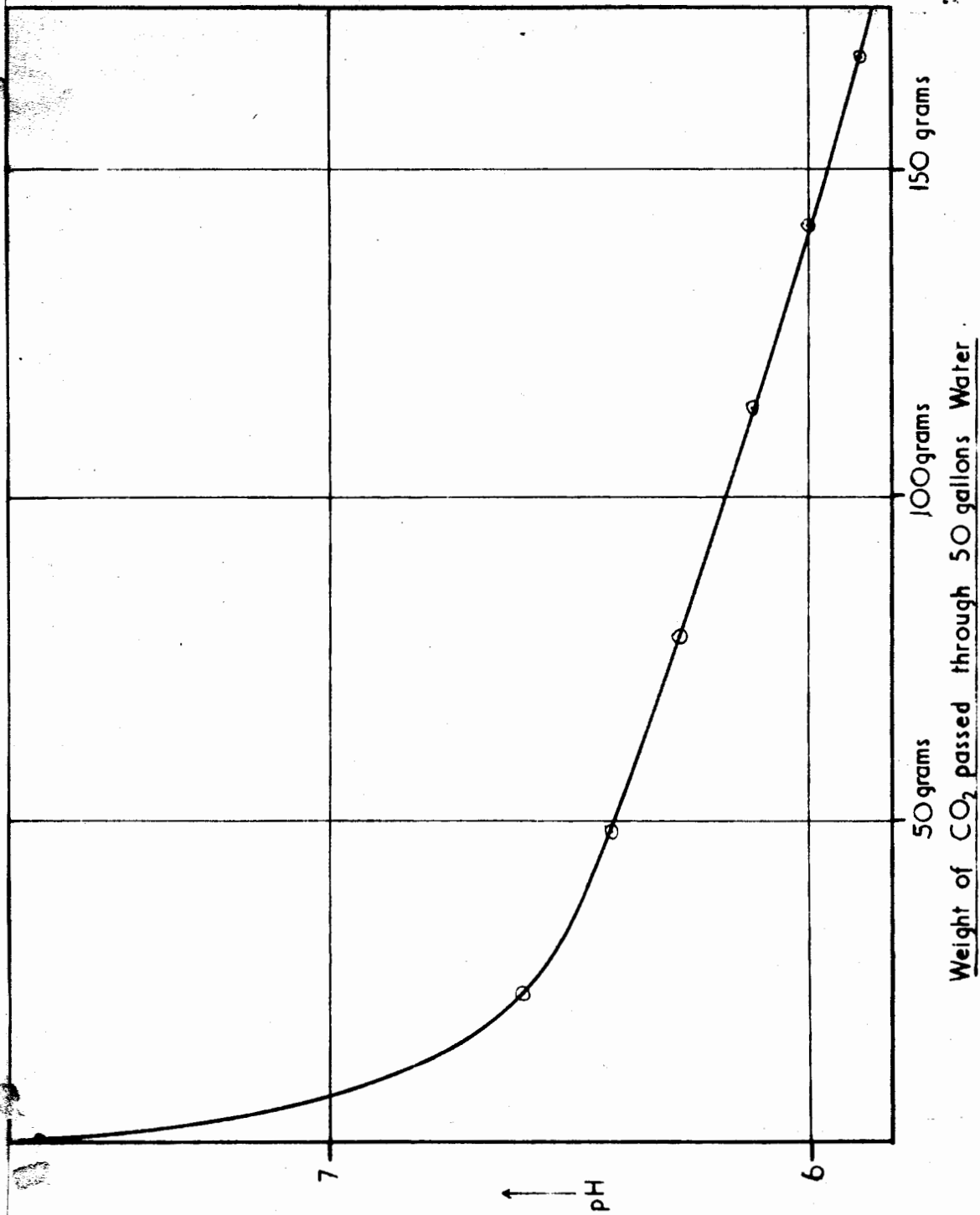
FIGURE 15. pH REDUCTION WITH CO_2

Observations

(a)   Efficient defluoridation was obtainable only when
the acid equivalents available were sufficient to neutralise
the hydroxide ions liberated.   Thus at 10 p.p.m. of fluoride
ion in the influent the type of acid did not affect
defluoridation materially.   Defluoridation of water containing
100 p.p.m. of fluoride ion was, however, accompanied by
liberation of more hydroxide ions than could be neutralised by
the acid equivalents available from the stronger acids at the
critical pH 5.5.   As a result, the pH value of the bed rose
rapidly with consequent inefficient defluoridation.

(b)   Results recorded in Table XVIII clearly illustrate the
advantage of carbonic acid over other types of acids,
particularly when the fluoride ion concentration is high.
The carbonic acid does not react with the alkalinity of the
water and its reaction with hydroxide ion, in the exchange
column, is to the bicarbonate stage only.   In the higher ranges
of fluoride concentrations therefore, the presence of dissolved
carbon dioxide in the influent is essential for efficiency.
Although addition of any acid to alkaline water, such as is
generally obtained from underground, will liberate carbon
dioxide in solution, it is obvious that except in cases of
exceptionally high alkalinity the quantity of acid required
for the desired decrease of pH will liberate insufficient
carbon dioxide for defluoridation of high concentrations of
fluoride ion.   During the present experiments acidification
by means of carbon dioxide was found most convenient and
effective.   Moreover, the acid requirements can be obtained
without a lowering of pH value to the critical level as in
the case of the other acids used in the above tests.

C,3. Regeneration of Exhausted Media

         As indicated before (refer III B 2 of this Chapter)

it was necessary to raise the pH value of the filter bed
in order to make the defluoridant exchange fluoride ions for
hydroxide ions. For this purpose a dilute solution of sodium
hydroxide was passed upwards through the filter. In order to
minimise dilution and effect maximum rise in pH, all water was
drained from the filter before introducing sodium hydroxide
solution at a rate of about 1 gallon/minute. The upward
passage of the solution caused a 40% expansion of the bed which
was found essential for efficient contact. When the requisite
amount of solution had been passed through, it was followed by
a continuous water rinse - the sodium hydroxide solution being
displaced upwards. Any turbidity which occurred, due to
attrition of the defluoridant granules, was removed in the
overflow. On recommencing defluoridation a volume of water
equivalent to the liquid content of the filter was run to
waste.

Regeneration was evaluated over some 20
regeneration cycles. The results are recorded in Table XIX.

No, of cycle.	NaOH re-cycle Quant. galle	Remarks
1	Fresh]	Shallow filter caused inefficient defluoridation.
2	25	
3	20	Defluoridant transferred to long perspex filter.
4	20	
5	20	High alkalinity of bed caused inefficiency.
6	20	Filter easily blocked.
7	15	Defluoridising
8	15	water containing
9	10	100 p.p.m. of
10	10	fluoride ion to a
11	15	concentration of
12	15	1.4 p.p.m. while
14	20	investigating
15	15	most efficient
		method of
17	20	regeneration
18	15	
20	20	Low capacity due to inefficient regeneration.
21	20	

C.3.(a). Strength and Quantity of Regenerant

Efficient regeneration was obtained with a 1% solution of sodium hydroxide, subsequent defluoridation cycles yielding an average capacity of 3.8 mg. F⁻ per gram of defluoridant. The use of more concentrated solutions was unnecessary since the pH value obtainable with a 1% solution was sufficiently high (>12) for displacement of fluoride ions from the defluoridant (refer Fig. 12). Regeneration with 0.5% solution of sodium hydroxide reduced the subsequent defluoridising capacity of the bed by more than half. The use of sodium carbonate solution for regeneration is similarly not advisable, insufficient rise in pH value of the bed being obtained.

About 15 gallons of regenerating solution, equivalent to 5.5 ml./g. of defluoridant, yielded maximum subsequent defluoridising capacity per unit of sodium hydroxide used. The use of only 10 gallons of regenerating solution resulted in a reduction in capacity which was not commensurate with the saving in regenerant. On the other hand, the increased capacity resulting from the use of 20 gallons was not in proportion to the increased consumption of regenerant.

C.3.(b). Method and Mechanism of Regeneration

Samples of the regenerant and wash water overflowing from the filter were taken at 4-gallon intervals (the approximate inter-spacial liquid volume of the filter) and analysed for fluoride content, alkalinity and pH value. These values were plotted against volume of liquid passed through as indicated in Fig. 16.
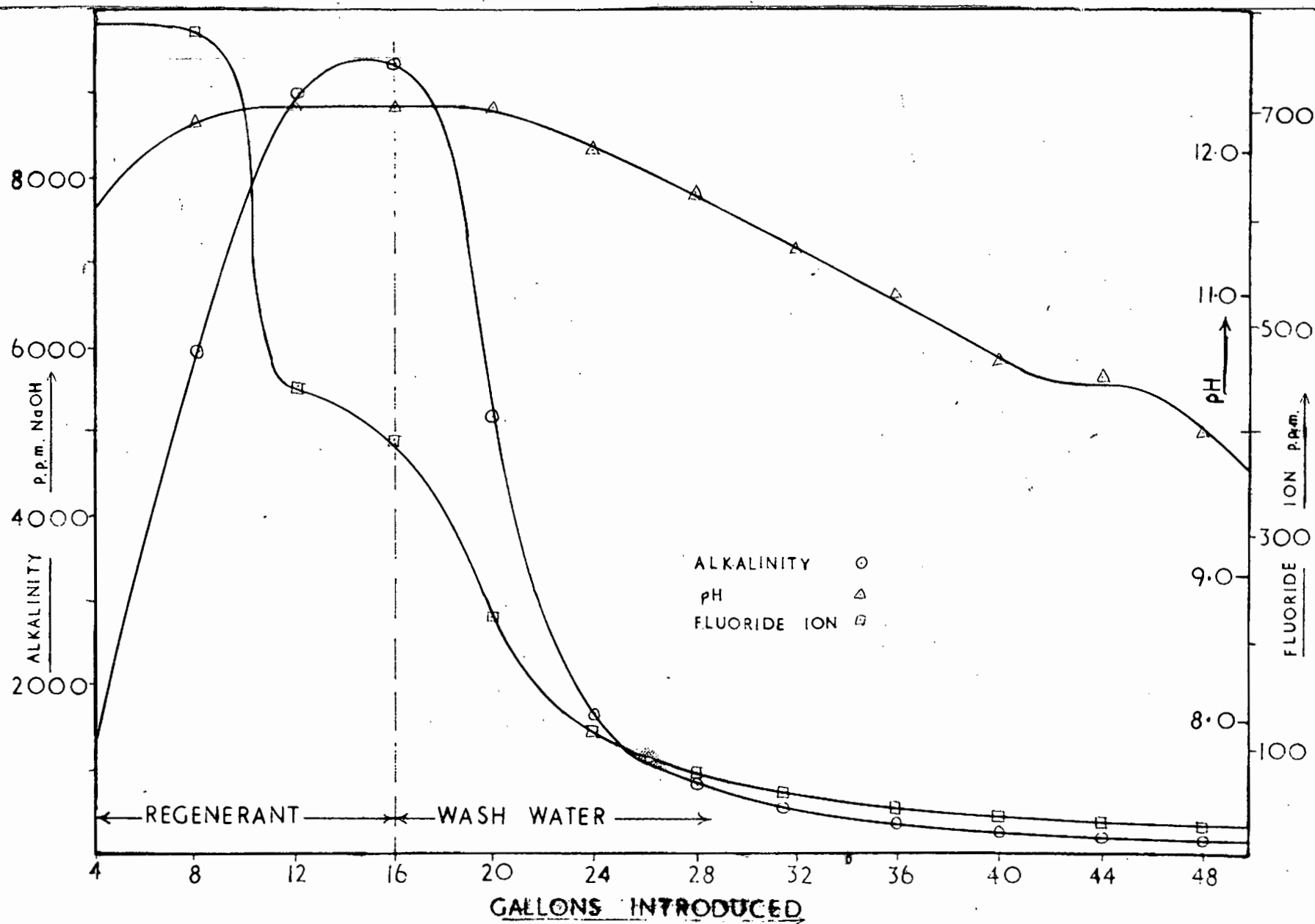
Figure 16   REGENERATION CYCLE   Nº 13

117.

Observations

(i)   On introducing the regenerating solution (a 1%
solution of sodium hydroxide, i.e. 10,000 p.p.m. NaOH), the
pH value of the bed rose rapidly, the hydroxide alkalinity
of the regenerating solution was reduced by 85%, while the
fluoride ion concentration of the liquid reached a maximum
immediately, in accordance with the reversible reaction for
regeneration :-

$$CaF.Ca_4(PO_4)_3 + OH^- \rightleftharpoons CaOH.Ca_4(PO_4)_3 + F^-$$

(ii)   With the introduction of more regenerant, fluoride ion
concentration decreased and hydroxide alkalinity increased,
indicating that superficial regeneration of the defluoridant
granules had been accomplished with consequent decrease in the
rate of ion exchange.   At this stage fluoride removal from
solid phase could, of course, be enhanced by allowing a longer
contact time between regenerant and defluoridant.   It was thus
found advantageous to retain the final portion of regenerant
in the filter for one hour before the water rinse was commenced.
The resultant increase in fluoride content of the regenerant is
clearly depicted in Fig. 16. (See also "Effect of Contact Time"
III, C, 3, c of this chapter)

(iii)   During subsequent backwashing with water at the rate
of 1 gallon per minute, the pH value of the overflowing wash
water (Fig. 16) decreased very slowly.   It was difficult
to remove adsorbed alkalinity from the bed, whereas about 8 ml.
of wash water/gram of defluoridant were used in the laboratory
trials, the pilot plant filter required at least 40 gallons,
equivalent to 14 ml./g. of defluoridant.

(iv)   The volume of wash water was subsequently reduced
by effecting the final neutralisation of adsorbed alkalinity
via controlled acidification of the feed water as indicated
above.

C3 (c) Effect of Contact Time

A longer contact time between defluoridant and regenerant increased the fluoride ion concentration in the regenerating solution and resulted in an improved defluoridising capacity.(Table XIX, Cycles 4 & 5, 7 & 8, 11 & 12). During cycles 16 & 17 it was attempted to determine the optimum contact time for regeneration. Regenerant was introduced in 5 gallon batches - each consecutive batch displacing the previous batch upwardly after 1 hour's soaking. Samples of each batch of regenerant were withdrawn from the filter shell at intervals during the soak period. The total volume of regenerant used was 20 gallons, and the results of analysis of the regenerating solution at various stages during cycle 17 are recorded in Table XX.

TABLE XX

QUANTITATIVE RECOVERY TESTS FOR FLUORIDE AND HYDROXIDE DURING REGENERATION

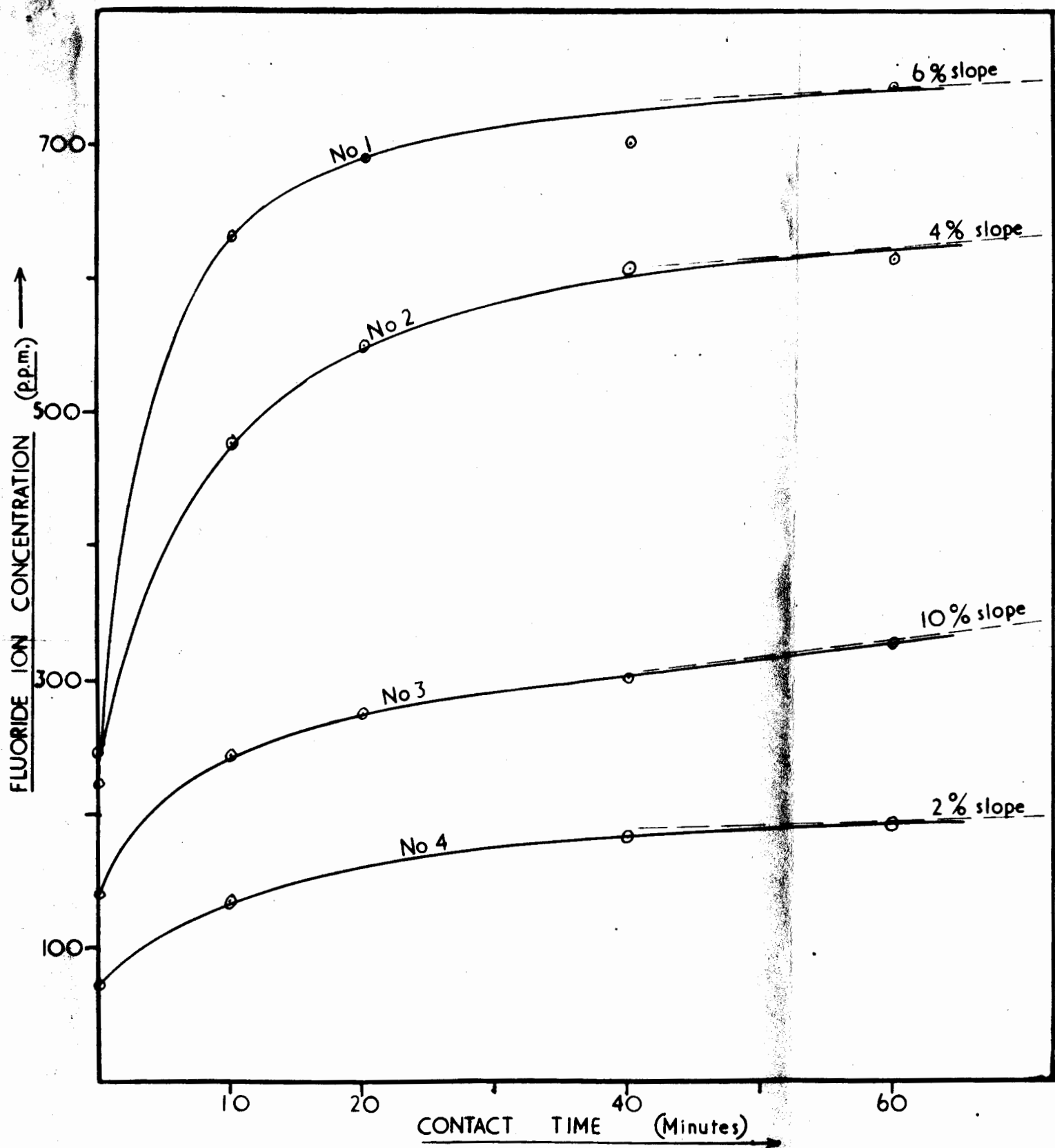| Batch Number (5 galls. regenerating solution)	Contact Time (Min)	Analysis		
		pH	Alkalinity % NaOH	F⁻ p.p.m.
1	Nil	12.40	0.758	222
	10	12.44	0.560	630
	20	12.47	0.543	690
	40	12.45	0.541	680
	60	12.43	0.529	740
2	Nil	12.50	0.905	245
	10	12.50	0.813	480
	20	12.49	0.771	550
	40	12.45	0.724	610
	60	12.44	0.697	610
3	Nil	12.52	0.970	140
	10	12.52	0.953	244
	20	12.50	0.941	276
	40	12.49	0.926	300
	60	12.48	0.925	325
4	Nil	12.53	0.991	76
	10	12.53	0.995	133
	20	12.49	0.978	162
	40	12.50	0.982	180
	60	12.49	0.971	190

Figure17 EFFECT OF SOAKING

The pH values of all the samples showed no significant fluctuations. The alkalinity of the regenerating solution dropped rapidly during the first and second fills due to a high rate of fluoride exchange as well as due to adsorption of hydroxide ions on the filter bed.

Fluoride ion concentration of the regenerant may be taken as a rough measure of the amount of regeneration obtained. When fluoride ion concentration in the regenerant is plotted against contact time as in figure 17, it is obvious that a minimum of 20 minutes should be allowed for each replacement of the filter. Equilibrium is not attained within this period but further increase of time is not justified by the extent of further fluoride removal obtainable.

The small amount of fluoride ion contained in the final batch of regenerant indicated that it might well be dispensed with and compensated for by an extended contact time for the third batch.

On the basis of these results it was concluded that maximum regeneration could be obtained by introducing regenerant in 3 successive batches, the volume of each batch being equivalent to the clear space plus the interparticle voids of the filter. The first two batches should have a contact time of 20 minutes each and the last batch 6 hours. The efficiency of this method of regeneration was borne out by subsequent cycles. (Refer cycles 17 and 18 in Table XIX). It was not feasible to introduce the regenerant at a continuous slow rate, equivalent to a contact time of 20 minutes since insufficient expansion of the filter bed as well as channelling resulted. Therefore, introduction of regenerating solution at a rate of 1 g.p.m. was used throughout.

For 20 regeneration and defluoridation cycles the average fluoride removal capacity of the defluoridant was 3.5 mg./g., taken within the limit of critical fluoride ion concentration (1 p.p.m.) in the effluent. The exchange capacity of the material is normally higher but as the latter becomes more saturated, it can no longer reduce fluoride ion concentration sufficiently and regeneration therefore ensues before complete saturation.

On continuous use of the defluoridant a slight decrease of capacity occurred. (Refer Table XlX). Since a quantity of defluoridant had been lost as a result of attrition, this decrease was ascribed to the reduction of volume of active material rather than to a net reduction of exchange capacity. Chemical degradation of the material can hardly be expected because the exchange reaction involves no change in the crystalline structure of the defluoridant. Moreover, the structure is such that it can only accommodate hydroxide or fluoride ions, hence its high selectivity in exchanging ions.

D. ATTRITION LOSSES.

Turbulence which occurred during backwashing, caused abrasion of defluoridant granules. The disintegrated particles were removed in the overflow during backwashing and represented a loss of active medium. Over the first 20 defluoridation and regeneration cycles of operation, the loss amounted to about 0.46% per cycle. In order to determine the loss more accurately, several further tests were undertaken.

D.1. Pilot Plant Filter.

The fluoride saturated defluoridant was backwashed continuosly without intermediate defluoridation. After passage of a quantity of liquid representing one regeneration cycle, the granules were allowed to settle for 2 minutes and their volume measured. Tap water, in some cases acidified with carbon dioxide, was used for backwashing at a rate of 1 gallon per minute. The results are depicted in figure 18.

The total loss of defluoridant over 59 cycles amounted to 11.27% or 0.19% per cycle. The loss was inversely proportional to the number of cycles, indicating that a hard granular core is left after initial surface attrition has taken place. (The average loss over the last 39 cycles was only 0.06% per cycle.) It would seem feasible that granules consisting of such hard cores only, may be prepared by providing adequate agitation during manufacture.

The use of acidified water with pH values of 5.5 to 6.0 did not affect the disintegration of the granules.

D.2. Laboratory Filter.

A quantity of defluoridant granules was prepared from superphosphate in the usual manner, but more violent agitation was employed. The mixture of superphosphate granules and excess 5% solution of sodium hydroxide was placed in bottles
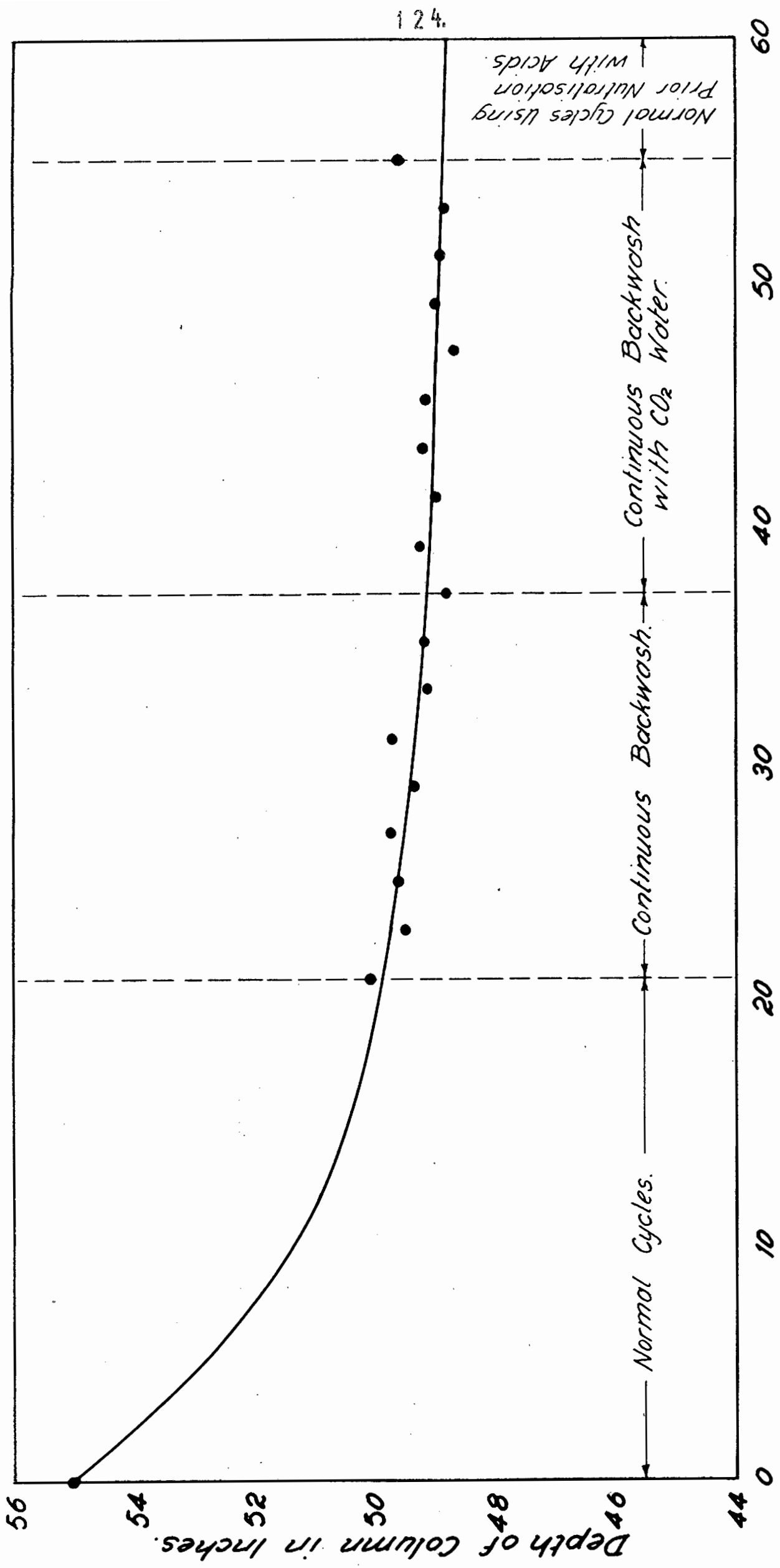
and/.......

Fig 18   Attrition loss in a Column of Defluoridont.

and rotated longitudinally at 19 r.p.m. for 24 hours. The
purpose of this treatment was to ensure that any soft
superficial layer on the granules would be removed, thus
yielding defluoridant granules with a high resistance to
abrasion. As a result a lower yield of defluoridant granules
was obtained, 57% as compared with 66% by the usual method of
intermittent gentle agitation. After adequate washing, one
part of the prepared granules was airdried at room temperature
while the other portion was tested directly.

For test purposes a filter was used which had
approximately the same ratio of diameter and depth as the plant
filter. Twenty-eight grams of the defluoridant were filled
into a tube of 2 cm. diameter to a depth of 20 cm. Ten litres
of distilled water were circulated upward through this bed at
70 ml./min. At this rate of backwashing the bed expanded 6 cm.
After circulation of a quantity equivalent to 175 regeneration
cycles, the granules were transferred from the filter and dried
and weighed. The loss incurred amounted to 18.3% or 0.10% per
cycle. The circulation water acquired turbidity equivalent to
1.5 p.p.m. SiO_2.

The air-dried granules had a moisture content of 9.7%
and were tested in a similar manner. Attrition loss amounted
to 19.8% over the equivalent of 48 regeneration cycles, i.e.
0.41% per cycle.

D,3. Standard Attrition Test.

The method of the American Water Works Association
Committee on specifications for zeolites (93) was used. The
test is based on measuring the turbidity produced by agitating
5 g. of medium with 50 ml. distilled water on a wheel rotating
at about 17 r.p.m. In the present test 2 samples each, of both
wet and air-dried defluoridant granules, were used. The
mixtures of granules and water were contained in bottles of 2"
diameter x 4¼" high and were rotated longitudinally at 18.62

r.p.m. .../

r.p.m. Turbidity was measured at 4 hour intervals with a "Hellige turbidimeter" as p.p.m. of SiO_2. After 16 hours agitation the granules were recovered, washed, dried and weighed. For purpose of comparison, samples of "Permutit" natural zeolite (green sand) and "zeokarb Na" were tested similarly. The results are recorded in Table XXI. (average values are given)

TABLE XXI

ATTRITION LOSSES OF ION EXCHANGE MATERIALS

Sample	Turbidity of supernatent water as p.p.m. of SiO_2.				% loss in weight of solid media.
	4 hrs.	8 hrs.	12 hrs.	16 hrs.	
Defluoridant (wet)......	180	260	380	470	6.4
Defluoridant (dry)	240	385	485	550	15.5
Natural zeolite...	47	68	-	-	0.2
Zeokarb Na.	600	800	-	-	7.9

D. 4. Discussion.

These tests indicate that the core of activated superphosphate granules is very much harder than the powdery surface layer. If, therefore, provision is made in the preparation of these granules to retain only the hard cores, a product is obtained whose resistance to abrasion compares favourably with that of "Permutit Zeokarb Na". Such abrasion resistant granules may be prepared by continuous agitation with the activating solution in a rotating container.

Passage of water acidified to a pH value of 5.5 did not effect the disintegration of defluoridant granules in a filter bed. It may, therefore, be concluded that attrition losses are entirely due to mechanical abrasion. Repeated defluoridation and regeneration cycles have also not revealed any chemical deterioration of the defluoridant granules.

Drying ../

Drying of the granules causes a definite weakening of the structure. It would therefore be best to store and transport the defluoridant under damp conditions. About 60% moisture content would be suitable.

The loss in weight observed in the laboratory filter and the standard abrasion test seems unduly high for the slight turbidity produced. The discrepancy is probable due to dissolution of calcium sulphate which is retained in freshly prepared defluoridant granules. In previous defluoridation experiments (refer 111 B, 1 of this Chapter) it was observed that sulphate was being dissolved by the filtrate during initial operation of a defluoridant bed.

The net loss in weight attributable to attrition is therefore considerably less than the recorded values. Calculations based on the solubility of calcium sulphate suggest a 50% reduction of the latter.

IV. HOUSEHOLD DEFLUORIDATION.

From the previous discussion under part 111, it is clear that defluoridation filter installations necessitate considerable capital outlay as well as skilled supervision. As such, it is more applicable to larger communities, rather than to individual households. For the latter purpose the use of defluoridant additives would be preferable. Furhter disadvantages of activated superphosphate filters are, the large losses incurred during separation and manufacture of granules from commercial superphosphate, the irregular size gradation, and the low mechanical strength of the granules. In order to obviate these difficulties, tests were undertaken to evaluate the efficiency of defluoridant powders which could be used as additves. For filter installations the use of "Saaifos" was investigated. "Saaifos" is the trade name for a granular fertiliser produced by partial neutralisation of superphosphate of lime, with ammonia. It became available in South Africa, only, after completion of the work already

described, but its special features viz granular form and partial neutralisation i.e. partial activation, encouraged its use.

A. ACTIVATED SAAIFOS FILTERS.

Granules of "Saaifos" -10, 450 mesh, were treated and tested in similar manner to superphosphate. It was found that "Saaifos" responded equally well to activation and defluoridation, although its defluoridising capacity was somewhat lower than that of activated superphosphate viz 2.0 and 3.5 mg./g. respectively. This lowered capacity was probably due to the less porous nature of "Saaifos" granules which resembled rolled spheres. These granules were much harder than the incidental superphosphate granules and consequently they suffered very little attrition loss during preparation and regeneration. The behaviour of this medium was identical to that of activated superphosphate in all other respects.

Since the acidity of superphosphate is partially neutralised during manufacture of "Saaifos", it was considered possible to activate the latter in situ in a filter column. It was found that the low porosity of the granules necessitated a longer soaking period, about 4 days, in a 5% sodium hydroxide solution. Considerable advantage is, however, to be gained from this method of activation.

On the whole the superior mechanical strength of "Saaifos" granules coupled with the fact that it is commercially available in granular form, makes its use most attractive.

This material was subsequently used in the large scale defluoridation plant mentioned in the introduction to this chapter It was activated in situ in a filter column of 15" diameter x 14 feet high and proved to be most satisfactory. This plant has been operated independantly since January 1956. It supplies 2000 g.p.d. of defluoridated water for domestic use.

B. ../

B. ADDITIVE DEFLUORIDANTS.

Phosphatic defluoridant powders, prepared by three different methods were evaluated. Theoretically any of the preparations listed in Table XII could be used for batch defluoridation, but economic considerations necessitate the use of commercial superphosphate derivatives only.

B,1. Preparation. Activated superphosphate and "Saaifos" media were prepared as described under II, C, 1, of this Chapter, except that the material was finely crushed before activation and that it was allowed to settle completely before decanting the supernatent activation liquor. During activation the materials sustained weight losses on a dry basis of 30% and 25% respectively.

A third medium was prepared by adding an aqueous solution of superphosphate to the requisite amount of milk of lime with constant stirring. The resulting precipitate was then washed free of soluble salts. By this method of preparation 100 grams superphosphate yielded 34.7 grams precipitate i.e. 65.3% loss in weight was sustained.

All three media were kept under moist conditions after preparation, since drying destroyed their activity as indicated under II, B, 2, of this Chapter.

B, 2. Defluoridation. The different media were intimately contacted with the water to be defluoridised by instantaneous shaking. They were thereafter allowed to settle and the clear supernatent liquids were decanted and analysed for fluoride ion. About 4 grams of each medium were thus mixed with successive 200 ml. aliquots of tap water containing 10 p.p.m. of fluoride ion and sufficient acid to control the pH value of the mixture at an optimum, between 7 and 8. The

residual ../

residual fluoride ion concentration in the supernatent water,
did of course increase gradually with successive batches and
when it exceeded 1.5 p.p.m. the defluoridant was considered
to be saturated.   No attempt was made to regenerate the
media.   The results of these tests are recorded in table XXII.

<div align="center">TABLE XXII</div>

<div align="center">DEFLUORIDISING CAPACITY OF ADDITIVE DEFLUORIDANTS</div>

Property	Activated super-phosphate	Activated "Saaifos"	Precipitated tri-calcium phosphate
Lowest Residual $[F^-]$p.p.m.	1.2	0.7	0.5
Capacity (mg.F^-/g. dry defluoridant)	3.4	3.8	10.1
Capacity (mg.F^-/g. of raw "super")	2.4	2.8	3.5
Acid used for defluori-dation (g.HCl/l. of raw water)	0.045	0.045	0.045
Average pH of supernatent	8.0	8.1	9.4

Observations: (a) From table XXII it is clear that all three
preparations could be used as additive defluoridants.   Their
order of efficiency is as follows: (i) precipitated tricalcium
phosphate, (ii) activated "Saaifos", (iii) activated superphosphate.

(b) The high defluoridising capacity of the
precipitate was largely offset by the high loss sustained during
its preparation.

(c) It was necessary to acidify the raw water prior
to addition of defluoridant. Tests showed that any acid could be
used for this purpose provided that sufficient reduction of pH
value was obtained.

(d) The pH value of the treated water was always
within the potable range.

(e) The quantity of defluoridant to be added to a
batch of water had to be in proportion to the quantity of fluoride

<div align="right">to ../</div>

to be removed, so as not to exceed the capacity of the defluoridant.

(f) The defluoridant had to be stored and added in moist form. A pulp with about 60% moisture was found suitable.

C. RECOMMENDATIONS.

The most suitable method of defluoridation of a specific water supply depends largely upon its quality. Thus, hard waters which require conventional lime-soda softening will generally have their fluoride concentration reduced to potable levels by the softening process. (77, 94 and II, A of this Chapter). High fluoride concentrations which always occur in soft waters can similarly be reduced to values of less than 10 p.p.m. by simple addition of lime, fluoride being precipitated as calcium fluoride. However, the further removal of fluoride to less than 1.5 p.p.m. requires treatment by the methods of the present investigation.

For defluoridation of fairly large supplies (>10,000 gallons per day) a filter installation utilising activated superphosphate or "Saaifos" granules and equipped with regeneration facilities is recommended. The cost of construction and supervision is in such cases justified by the volume of water to be treated.

For smaller supplies especially as are required by individual households, the use of defluoridant additives is preferable. Such media may be made available in packaged form, each package being sufficient for a definite volume of water. By this method of treatment the risk of inefficient defluorida-tion with an exhausted filter would be largely eliminated, since each batch of water would require a fresh addition of defluoridant whereas a small defluoridation filter may be easily neglected to the stage where defluoridation will no longer proceed.

Defluoridant .../

Defluoridant media may be prepared as described
in this thesis and made available as a commercial commodity,
so as to be used wherever it is required.

Note. Patent cover for the manufacture and use of this activated
phosphate has been obtained and the patent rights have been
ceded to the S.A. Council for Scientific and Industrial Research.

D. COSTS.

The most important result of the present investigations
is that an economical method of defluoridation of water has been
developed. Estimates of the cost are as follows:-

The cost of superphosphate in South Africa is about
£12.10.0. per short ton, while sodium hydroxide costs about £40
per short ton. The raw materials required to produce 1 ton of
activated superphosphate defluoridant would thus cost

$$(£12.5 + 0.32 \times £40) \times \frac{1}{50\%}$$

where 0.32 = grams NaOH used per gram super

& 50% = yield of defluoridant.

i.e. cost = about £50.

If it is assumed that labour and marketing would cost
another £50 per ton the final cost of the defluoridant need not
be more than 1 shilling per lb. This compares most favourably
with the cost of alternative defluoridants which are estimated
to cost about 10/- per lb. in the United States of America (95).

A further detailed investigation (96) of plant
construction and operational costs has indicated that large
scale defluoridation of water by means of activated superphosphate
filters would cost about 1.3 shillings per 1000 galls. This
cost should be well within reach of most South African communities.
Small scale batch defluoridation has been estimated to cost 1.5
pence per 10 gallons of water.

Defluoridation of water has thus become a practical
feasibility to all who have hitherto suffered the ill-effects of
excessive fluoride ingestion.

_____ oOo _____

1. The demineralisation of saline water is receiving an increasing amount of attention all over the world.

2. In South Africa, fresh water supplies are limited and at present saline waters containing more than 2,500 p.p.m. of dissolved salts are being used by at least 150 communities and numerous individual farms, with possible deleterious effects upon the health of men and beasts.

3. Waters containing harmful concentrations of fluoride ($\geqslant$ 1.5 p.p.m.) are also being used extensively due to the unsuitability of existing defluoridation methods.

4. Various methods of demineralisation and defluoridation were critically reveiwed, especially with regard to cost and practical feasibility.

5. In South Africa, demineralisation by means of solar distillation is attractive because plenty of sunshine is available in the many arid regions: where small household supplies only, are required.

6. A programme of research was undertaken with an experimental solar still of 16 sq.ft. pan area, in order to correlate distillation efficiency with   local climatic conditions.

7. An average daily yield of 0.762 Imp. gallons was obtained, equivalent to a 30% utilisation of the solar radiation impinging on the still.

8. Ambient and saline water temperatures were found to have an important bearing upon the efficiency of distillation. This observation has apparently not received the attention of workers elsewhere.

9. An equation, based on experimental data, was formulated to relate the thermal efficiency of the still with atmospheric temperature.

10. The influence of winds, rain, humidity and pressure was mainly indirect as manifested in temperature and radiation changes.

11. Improved distillation was obtained from the use of mirrors and artificial cooling of condenser surface but their cost does not appear to be warranted.

12.8 Sufficient data was obtained to indicate a suitable design of household still and to estimate costs.

13. The efficiency of various methods of defluoridation were assessed. For this purpose the numerous methods of fluoride determination in water, were critically reviewed.

14. The method described by Stevens was found most suitable for direct routine estimation of fluoride ion concentration, while the standard distillation method was used as an intermittent check on the former method.

15. Flocculent precipitates will absorb fluoride from water, but the removal was found to be incomplete and impracticable.

16. Precipitated calcium phosphates were excellent defluoridants but several disadvatages rendered them unsuitable for practical application in columns.

17. A cheap and efficient defluoridant was prepared by simple treatment of superphosphate of lime with excess dilute sodium hydroxide solution.

18. Such activated superphosphate consists chiefly of micro-crystalline apatite which exchanges hydroxide ion selectively for fluoride ion. The exchange appears to be effected only on the surface of the crystals.

19. Granules of activated superphosphate were used successfully in conventional ion exchange type filters for defluoridation of fluoride bearing water. The average defluoridising capacity of the material was 3.5 mg. F^- per gram, taken within the range of fluoride reduction to the optimum limit.

20. The ion exchange properties of the defluoridant are critically controlled by changes in pH value. At pH values above 12 fluoride ions are exchanged for hydroxyl ions and at pH values between 6 and 8 defluoridation of water in contact with it proceeds rapidly.

21. After saturation with fluoride ions, the defluoridant may be regenerated with a 1% solution of sodium hydroxide. The method of regeneration which was developed restores the fluoride capacity of the material and no defluoridised water is required for rinsing. A considerable saving of de-fluoridised water is thus attained.

22. Defluoridation of both household and public water supplies by means of activated superphosphate should be a practical feasibility.

1. Cillie, G.G., "The Problem of Water Supply on the West Coast of the Cape and in South West Africa" C.S.I.R. Internal Report, June 1950.

2. South African Bureau of Standards, "Specifications for Water for Domestic supplies", 1951.

3. Ockerse, T. "Endemic Fluorosis in South Africa", Published by S.A. Dept. of Public Health, 1946.

4. Eager, J. U. Pub. Health Rep., 16, 2576, (1901)

5. Churchill, H.V. 'Occurrence of Fluorides in Some Waters of the United States. Ind. Eng. Chem., 23:996 (1931).

6. Smith, M.C., Lantz, E.M. and Smith, H.V. "The Cause of Mottled Enamel, a Defect of Human Teeth." Univ. of Ariz. Exp. Sta. Tech. Bull., 32:253 (1931)

7. Velu, H. "Dystrophie Dentaire des Mammiferes des Zones Phosphates (Darmous) et Fluorose Chronique". Compt. rend. Soc. de Biol., 58:750 (1931).

8. Dean, H.T. and Elvove, E., Pub. Health Repts. 50, 1719 (1935).

9. Dean, H.T. and Elvove, E., "Some Epidemiological Aspects of Chronic Endemic Dental Fluorosis." Am. J. Pub. Health, 26:567 (1936).

10. Dean, H.T. and Elvove, E., Pub. Health Repts. 52, 1249 (1937).

11. Dean, H.T. and Elvove, E.,   ibid   54, 212 (1939).

12. Dean, H.T. et al.   ibid   54, 862 (1939).

13. Dean, H.T. et al.   ibid   56, 761 (1941).

14. Scott, D.B., Picard, R.G. and Wyckoff, R. W. G., Pub. Health Repts. 65, 43 (1950).

15. Kuntson, J.W., J. Dental Research 27, 340 (1948).

16. Bull, F.A., Pub. Health Eng. Abstracts 28, 27 (1948).

17. National Research Council Report, J. Am. Water Works Assoc. 44, 1 (1952).

18. Cox, C. R. and Ast, D.B.,   ibid 43, 641 (1951).

19. Faber, H.A., Water and Sew. Works, 98, 203 (1951).

20. Ockerse, T., "Dental Caries, Clinical & Experimental Investigations" (1949).

21. Steyn, D. G. and Reinach, N. "Water Poisoning in South Africa of Man and Animal". Onderstepoort J. of Vet. Sci., 12:167 (1939).

22. Wilson, D.C., Lancet, p.211 (Feb. 15, 1941).

23. Richter and MacLean, Amer. J. Physiol. (1939), 126, 1.

24. Whipple, G.C., "The value of pure water." Pub. by John Wiley and Son. Inc., 1907.

25. Sollman. T., Manual of pharmacology, 1942.

26. MacDougal, D.T., "Botanical features of North American deserts." Publication of the Carnegie Institute.No;99.

27. Suckling, E.V., "The examination of waters and water supplies." P.84→113. London, 1944.

28. Muehlberger, C.W., Water and Sewage Wrks., (1951), 98, 483.

29. Adams, B.A. and Holmes, E.L., J.Soc. Chem. Ind., 54, 1, (1935)

30. Aultman, W. W., J. Am. Water Works Ass., 42, 786, (1950)

31. Anon, Chem. Eng. News 27, 3306, (1949)

32. Buswell, A.M., U.S. Patent No. 2,522, 856 (Sept.1950)

33. Hult, W.A.E., U.S. Patent No. 2,546,071 (March 1951)

34. Cox, J.D., British Commonwealth Scientific Office (North America) Report No. 1022 April,1955.

35. Cox, J.D., British Commonwealth Scientific Office (North America) Report No. 1021, March,1955.

36. General Technical Department, T.N.O. Holland Report T.A. 270 (1952)

37. Wyllie, M.R.J. & Patnode, H.W., J. Phys & Colloid Chem., 54, 204, (1950)

38. Ionics Inc., "Permionic Membrane Demineralisation.", Bul. No. 2 (1952)

39. van Platen, B., U.S. Patent No. 2, 520, 186 (Aug.1950)

40. Murphy, G.W., Progress Report July-Sept. 1953, Saline Water Programme, U.S.Dept. of the Interior.

41. Claude, G. Power from the Tropical Sea. Mech.Eng.52, 1039. (1930).

42. Hottel, H.C. and Woertz, B.B. "Performance of Flat Plate Solar-heat collectors",Trans.Am.Soc. Mech.Eng., 64, 91, (1942).

43. Hollingsworth, F.N. "Solar Energy to Provide Water." Heating & Ventilating, 45, 99, (1948).

44. Harding, J., "Apparatus for Solar Distillation", Proc. Inst. Civil Eng., 73, 284, (1883)

45. Löf, G.O.G. "Demineralisation of Saline Water with Solar Energy" U.S. Dept. of the Interior, Saline Water Conversion Program, Progress Report No. 4. (Aug.1954)

46. Telkes, Maria, Ind. Eng. Chem., 45, 1108 (1953)

47.   Howe, E.D., Sea Water Conversion Program, Progress
        Report for the State of California Legislature.
        (March 1955).

48.   Rounds, G. , Saline Water Conversion Program of the
        U.S. Dept. of the Interior, Progress Report No.5.
        Febr. 1955.

49.   Löf, G.O.G., Personal Communication at the World
        Conference on Solar Energy (Arizona,Oct. 1955).

50.   Drummond, A.J. and van Deventer, E.N., Tydskrif vir
        Wetenskap en Kuns, X1V (2), 111, (1954).

51.   Cillie, G.G., "Defluoridation of Water Supplies"
        Chemistry and Industry, Aug.30, 1952.

52.   Beevers, C.A. and McIntire, D.B., "Crystal Structure
        of Apatites". Minerological Mag., $\underline{27}$, 254 (1946)

53.   Willard, H.H. & Horton, C.A., Ind.Eng.Chem. (Anal.),
                                        $\underline{22}$, 1190, (1950)

54.   Foster, M.D.   ibid., $\underline{5}$, 234, (1933)

55.   Boruff, C.S. & Abbott, G.B., ibid., $\underline{5}$, 236, (1933)

56.   de Boer, J.H., Chem. Weekblad, $\underline{21}$, 404 (1924).

57.   Pavelka, F., Mikrochemie, $\underline{6}$, 149 (1928).

58.   Feigl, F.,   ibid , $\underline{7}$, 13 (1929).

59.   Alamarin, Z. Anal.Chem. $\underline{81}$, 8 (1930).

60.   Willard, H.H. and Winter, O.B., Ind.Eng.Chem.
                (Anal.) $\underline{5}$, 7 (1933).

61.   Thompson, T.G. and Taylor, H.J., ibid $\underline{5}$, 87 (1933).

62.   Sanchis, J.M.,   ibid $\underline{6}$, 134 (1934).

63.   Reynolds, D.S. and Hill, W.L.   ibid $\underline{11}$, 21 (1939).

64.   Stevens, J.A., J.S.A. Chem. Inst. $\underline{1}$, 1 (1948).

65.   Copeman, P.R.v.d.R., S.A. Ind. Chem., $\underline{5}$. 236 (1951).

66.   Fahey, J.J., Ind. Eng. Chem. (Anal.) $\underline{11}$, 362 (1939).

67.   Thrun, W.E.   ibid $\underline{22}$, 918 (1950).

68.   Willard, H.H. and Horton, C.A.,   ibid $\underline{22}$, 1194 (1950).

69.   Deladrier, J.B. Chem.Weekblad, $\underline{21}$, 404, (1924)

70.   Pisani,   Compt.Rend. $\underline{162}$, 791, (1916)

71.   Wagner, & Ross Ind.Eng.Chem.$\underline{9}$, 1116 (1917)

72.   Reynolds, D.S. et.al. Ind.Eng.Chem.(Anal.) $\underline{3}$,366 (1931).

73.   Shuey, M., J.Ass. Official Agric.Chem., $\underline{14}$, 126 (1931).

74.   Hill, H.J. and Reynolds, C.A., Ind. Eng. Chem. (Anal.)
                $\underline{22}$, 451, (1950).

Prepa-ration	Method of Regeneration	%F re-covered during Regene-ration	Defluoridising capacity mg/gram	Lowest residual F con-centra-tion ob-tained p.p.m.	Dissolution of PO$_4^{---}$	Remarks
3.5 CaCl$_2$ + (2 Na$_3$PO$_4$ + 2 NaOH mixture)	Freshly prepared material		10.8	zero		
	1st Regeneration 40 ml. 5% NaCl	11	2.7	3.2	zero	
	2nd Regeneration 40 ml. 5% NaCl	49	2.0	4.8	zero	Discarded
	1st Regeneration:20 ml. 5% CaCl$_2$ + 1.5 ml. 5% NaOH	Nil	0.6	8.4	zero	Regeneration caused colloidal dispersion
	2nd Regeneration:20 ml. 5% NaOH	60	2.9	2.8	+	Dissolution of phos-phate renders process impracticable.
	1st Regeneration:20 ml. 5% NaOH	23	2.8	3.0	+	Dissolution of phos-phate renders process impracticable.
	2nd Regeneration:20 ml. 5% NaOh	91	2.6	3.4	+	Dissolution of phos-phate renders process impracticable.
	3rd Regeneration:20 ml. 5% NaOH	104	3.0	2.4	+	Dissolution of phos-phate renders process impracticable.
	4th Regeneration:20 ml. 5% NaOH	68	2.7	3.2	+	Dissolution of phos-phate renders process impracticable.
3.5 CaCl$_2$ + (2Na$_3$PO$_4$ + 1 NaOH mixture)	Freshly prepared material		11.0	0.1		
	1st Regeneration:10 ml. 1% NaOH	80	5.4	1.0	+	Dissolution of phos-
	2nd Regeneration:10 ml. 1% NaOH	65	1.8	1.0	+	phate renders process
	3rd Regeneration:10 ml. 1% NaOH	53	0.9	1.4	+	impracticable.

75. American Public Health Ass. "Standard Methods for the Examination of Water & Sewage", Ninth Ed. p.77, (1946).

76. Rickson, J.B., Analyst, 75, 85, (1950)

77. Scott, R.D., Kimberley, A.S., van Horn, A.L., Ey, L.F. and Waring, F.H. "Fluoride in Ohio Water Supplies - Its Effect, Occurrence and Reduction". J. Am. Water Works Ass., 29:9 (1937).

78. Zettlemoyer, A.C., Zettlemoyer, E.A. and Walker, W.C. "Active Magnesia. 11. Adsorption of Fluoride from Aqueous Solution." J. Am. Chem. Soc., 69:1312 (1947).

79. Goetz, P.C. and Tiger, H.L. U.S. Patent No.2,428,418 (Oct., 1947).

80. Boruff, C.S. "Removal of Fluorides from Drinking Waters." Ind. Eng. Chem., 26:69 (1934).

81. Swope, H.G. and Hess, R.H. "Removal of Fluorides from Natural Waters by Defluorite." ibid. 29:425 (1937).

82. Marks and Clerk. Br. Patent 569,307 (May, 1945).

83. Maier, F.J. U.S. Patent 2,531,451 (1950).

84. McKee, R.H. and Johnston, W.S. "Removal of Fluorides from Drinking Water". Ind. Eng. Chem. 26:849 (1934).

85. Smith, H.V. and Smith, M.C. "Bone Contact Removes Fluorine." W.W. Eng., 90:1600 (1937)

86. Elvove, E. "Removal of Fluoride from Water." Pub. Health Rept., 52:1308 (1937).

87. Adler, H., Klein, G. and Lindsay, F.K. "Removal of Fluorides from Potable Water by Tricalcium Phosphates." Ind. Eng. Chem., 30:163 (1938).

88. MacIntire, W.H. and Hammond, J.W. "Removal of Fluorides from Natural Water by Calcium Phosphates." ibid., 30:160 (1938).

89. Behrman, A.S. and Gustafson, H. "Removal of Fluorides from Water." ibid., 30:1011 (1938).

90. Goodwin, R.C. and Litton, J.B. "Removal of Fluorides from Public Water Supplies." ibid., 33:1046 (1941).

91. van der Merwe, P.K. "The Removal of Fluorine from the Drinking Water of Children." Farming in South Africa, 15:360 (1940).

92. Hodge, H.C., LeFevre, M.L. and Bale, W.F. "Chemical and X-ray Diffraction Studies of Calcium Phosphates." Ind. Eng. Chem. (Anal. Ed.), 10:156 (1938).

93. Broderick, S.J. and Hertzog, E.S. "Determination of Attrition Loss of Carbonaceous Zeolites." J. Am. Water Works Ass., 34:94 (1942).

94. Maier F.J. Am. J. Pub. Health, 37, 1559 (1947).

95. Maier, F.J., Personal Communication. (1955)

96. Cillie, G.G., "Practical Defluoridation" C.S.I.R. Internal Report (1955).

1941, Graduated B.Sc. Applied & Industrial
Chemistry at the University of Cape Town.

1942 + 1943, Chemist - Superintendent on the Gun- Cotton
plant of Messrs. Cape Explosives Works at
Somerset West.

1944-Aug., Research Chemist in charge of testing & pro-
  1947, cessing of fish & fish products at Messrs.
National Trawling & Fishing Co.,Ltd., of
Cape Town.

1947,Sept., Research Officer in charge of Chemical Liaison
for the Council for Scientific & Industrial
Research.

1950,April, Transfered to Water Research Division.

1952,April, Promoted to Senior Research Officer.

1955,Aug., Biochemist for the Municipality of Paarl.

1955, Nov. Delegate to World Symposium on Applied Solar
Energy, Arizona, U.S.A.

PUBLICATIONS

1. "The Possibilities of a Citric Acid Fermentation
Industry in the Union of South Africa". South
African Industrial Chemist, February, 1949.

2. "The Preservation of Jute Bags" South African In-
dustrial Chemist, December, 1949.

3. "The Problem of Water Supply on the West Coast of
the Cape and in South West Africa". C.S.I.R.
Internal Report, June, 1950.

4. "Occurrence of an Amylopectin in the Fruit of the
Granadilla (Passiflora Edulis)" Journal of the
Science of Food an Agriculture December,1950.

5. "Pectin: Its possible Manufacture in South Africa"
Food Industries of South Africa, January, 1951.

6. "The Treatment of Tannery Effluents"
Municipal Affairs: November, 1951.

7. "The Quality Requirements of Water for Domestic Use"
South African Industrial Chemist, June, 1952.

8. "Defluoridation of Water Supplies Using an Activated
Superphospate" Chemistry & Industry, August,30,
1952.

9. "Defluoridation of Water Supplies"
C.S.I.R. Internal Report, June 1954.

10. "Solar Distillation of Saline Waters"
C.S.I.R. Publication, July 1955.