SECTION I

INTRODUCTION

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SECTION I

INTRODUCTION

A) POTASSIUM RESOURCES & REQUIREMENTS IN INDIA

Potassium salts are among the essential plant nutrients. The intensive use of nitrogeneous fertilizers requires application of large quantities of potash fertilizers either as chloride, sulphate, nitrate or phosphate. Potassium fertilizer has important function in the formation of carbohydrates and is deemed essential for oil and albuminoid synthesis, for development of chlorophyll and for efficient photosynthesis. It offsets an over supply of nitrogen and helps the plant to reduce transpiration. It also helps the plant to develop resistance against attacks by pest, rot fungi and various insects. The crops like sugar, tobacco, cotton, paddy, potato remove potassium from soil requiring large quantities of potassium fertilizers for replenishments. Besides potassium chloride as a fertiliser, it is the starting raw material for manufacture of many potassium chemicals used in commerce. Potassium chlorate and nitrate are of military importance for their use in explosives; potassium hydroxide, carbonate are used for soap, glass and textile trade; while potassium ferri and ferrocyanides are used in dyeing calicoprinting industries. Thus potassium is both wealth and weapon.

Worlds demand and supply of potassium:

The greater proportion of the world's demand for the potassium salts is met from bedded deposits, chiefly as chloride or sulphate. The average composition of igneous rocks contains following percentage of alkali metals

Na 2.85, K 2.6, Li 4×10^{-5}, Rb 1×10^{-6}; Cs 1×10^{-7} (grams per tonne). The concentration of sodium and potassium in sea water is Na 10.6 g and K 380 mg per litre. The Ratio of potassium to sodium is changed from the first only because of the absorption of potassium ions by plants and soil.

Bedded deposits -

Germany - The Stassfurt deposits has been worked extensively. German potash deposits in middle Rhine, Hannover, Southern Baden Harz are known to everybody. As a result of division of Germany, the production of potassium is also divided, 61 per cent Russian zone, 22 per cent British zone, 14 per cent American zone and 3 per cent French zone. In 1958 Federal Republic has produced 16401000 tonnes of potash salts containing 1987000 tonnes K_2O while eastern Germany produced 1624000 tonnes K_2O. The overall production is well over 3611000 tonnes K_2O.

France - Main deposits are in Alsace which contain two layers 0.8 and 0.3 meter thick separated by a layer of 1.8 meter shale of rock salt. The analysis reports 23 to 25 per cent potassium chloride while the rest is sodium chloride and insoluble matter. Alsaee mines are expected to rise to a production of 9 lakh tonnes of potassium chloride annually in very near future.

United States - The main deposits are around New Mexico Midland country and Texas (Carlsbad). The seams range from 8 to 14 feet depth. The potash bearing strata extends over 3000 sq.miles and contains well over 1000 million tonnes of potassium salts.

Canada - Salt beds in Saskatchewan and adjacent Parts of Manitoba and Alberta all contain potash deposits. At the end of 1960 twelve companies holding 1750000 acres of potash land rights started working. In terms of K_2O two plants were expected to produce 2300,000 tonnes K_2O.

Spain - The potash minerals are mainly carnallite and sylvite, 3 to 24 feet thick beds are reported and reserves well over 300 million tonnes of K_2O.

Poland - Richest and extensive deposits are found near Kalusz in south east poland. Deposits are 350 to 1000 feet below the surface and the chief minerals found are sylvite and kainite; estimated reserves are well over 100 million tons containing 10 to 20 per cent K_2O.

Sicily and Java - Sicily beds contain 6 to 15 per cent K_2O. A plant at Campofranco is already working. Java's Murecial Volcano bears Lucite lephrites containing 5 per cent K_2O while in Finland Livaava mountains contain potassium deposits with other valuable minerals.

England - In north east Yorkshire near Shilay contains deposits of polyhalite, kerenite, sylvenite and carnallite below a depth of 4000 feet and deposits are not worked in normal times.

Russia - Wolikamsk deposits (Urals) are different from

Stassfurt deposits containing no sulphate ion. The thickness of carnallite beds ranges from 25 to 100 meters and sylvinite 15 - 30 meters. Prospecting data indicate a reserve of 6 billion tonnes of K_2O under an area of roughly 550 sq. meters.

Israel - It is the world's largest producer of potash salts from natural brines from Dead Sea. The contents of potassium chloride varies with the depth of brine. At surface it is 1 per cent which rises to 1.5 per cent at 300 feet below. In practice brine is pumped from 170 feet depth. Potassium is recovered by using solar energy.

Jordan - Arab Potash Co. Ltd.,X is working on the north side of Dead Sea. Detail production figures are not available.

Searles Lake, California (U.S.A.) - Potassium salts along with sodium carbonate, borax, sodium, lithium phosphate and bromine are produced in large quantities from Searles Lake.

Other sources of potassium (1) Wood ashes - The ash of wood contains about 30 per cent potassium carbonate. In Caucasus the sunflower is grown on waste land for the sake of collection of seeds. The stalks and leaves are burnt, and the ashes are used as a source of potash. Nearly 7000 tonnes per year, crude potash from this source alone is exported from Norovossik in Russia. Residues in manufacture of olive oil and almond shells are rich in potassium salts. Roots of water hycinth(richornia Crassipes) furnishes 15 per cent ash containing 25 per cent K_2O. Banana skins furnish

1.77 per cent ash containing 57 per cent potash. Ashes from certain normal crops are Grain 14.39 Straw 32.73, Roots, 142.6, Tops 88.8, May 38.2 per cent K_2O per acre are reported.

2) Wool flat or suint - In wool washing with water the sweat or suint as it is called contains mainly potassium carbonate and fat. Potassium carbonate concentrates in the wash liquors which is further concentrated to recover potassium carbonate. About 30 kg. of potassium salts are obtained from 1000 kg of raw wool.

3) Cement Kiln & Blast furnace flue dust

Two systems are in vogue for the recovery of alkali from cement or blast furnace dust. (1) Electrical precipitation by Cottr$\overset{e}{a}$ll's process; (2) The water spray system. It is estimated that from England and Wales alone over 60,000 tonnes of potassium chloride per year is available from this source (30.2 lbs per million cubic feet of gas).

4) Sea weeds - In England certain sea weeds such as Laminaria on lixivation produces 10,000 tonnes of potash salts. In Indian species have shown the presence of potassium in (1) green algae - Ulva, Enteromorpha (2) Brown algae - Sargassum, Spathoglassum, Padina 3) red algae - Gracilaria, Gelidiella. The concentration varies from 2 to 5 per cent.

Requirement and Resources in India

India ~~is not having~~ does not have any large deposits of potassium salts except small quantities of salt petre-exuded in the soil of Uttar Pradesh, Bihar, Punjab and Madras. This accounts only for the annual production of 15000 tonnes of crude potassium nitrate. Potassium salts such as chloride, sulphate which are largely used as fertilizers are being imported, involving foreign exchange worth over Rs.2 crores. It is estimated that in the fourth five year plan period, 3 lakh tonnes of potassium fertilizer will have to be imported annually at the cost of Rs. 10 crores. Potassium consumptions in other countries such as U.S.A 2 million tonnes, West Germany 1 million tonnes, U.S.S.R 7 million tonnes and France 0.83 million tonnes are reported. Compared to these figures potassium consumption in the country is not significant and more and more needs may be felt in near future.

B) Composition and relationship of major constituents in sea-water

Sea water covers roughly 70 per cent of the earth's surface and may be considered as a dilute solution (3.5 per cent) containing a variety of dissolved solids and gases. Principal~~e~~ constituents in sea water are calcium carbonate, calcium sulphate (gypsum), sodium chloride, magnesium sulphate, magnesium chloride and potassium chloride. These major constituents present in sea water exhibit the property of constant relative proportions, that is variations in the composition of actual sea water are due to changes in the amount of water present. If the concentrations of various elements are classified (Table 1) as major, minor and trace elements,

Table 1 Sea water constituents (19.0 $^{o}/_{oo}$ chlorinity) and major constituents relationship with the total solids. ($34.4^{o}/_{oo}$ salinity) present in sea water.

MAJOR			MINOR			Trace (30 elements, important elements of the series)	
Element	Concentration (ppm)	Per cent salinity	Element	Concentration (ppm)	Per cent salinity	Element	Concentration (ppm)
1) Chlorine	18,980	55.2	7) Bromine	65	0.2	11) Lithium	0.1
2) Sodium	10,561	30.4	8) Carbon	28	-	12) Rubidium	0.1
3) Magnesium	1,272	3.7	9) Strontium	13	0.05	13) Iodine	0.05
4) Sulphur (as sulphate)	884 (2.650)	2.5 (7.7)	10) Boron	4.6	-	14) Copper	0.003
5) Calcium	400	1.2				15) Silver	0.0003
6) Potassium	380	1.1				16) Gold	0.000006

the major constituents are six, namely chlorine, sodium, magnesium, sulphur, calcium and potassium. The minor constituents with concentrations ranging between 1 and 100 ppm are four, bromine, carbon, strontium and boron. Trace elements ranging from 1 ppm downwards include lithium, rubidium, iodine, copper, silver etc. The concentrations of various constituents present in sea water, adjusted to a chlorinity of 19.00 $^{o}/_{oo}$, and the total dissolved solids, (salinity = 34.4 $^{o}/_{oo}$) are given in Table 1. Chlorine present as chloride ion is the most abundant ion and makes up about 55 per cent by weight of the dissolved material. Sodium is the next abundant cation in sea water and both together as sodium chloride comprise about 90.6 per cent of the total salts. The next important element is magnesium, whose ratio to the chlorinity is uniform. Sulphur is present in sea water as sulphate ion. Calcium is present in much smaller quantity than either sodium or magnesium. The distribution of calcium in the sea has been exhaustively studied mainly because it is a major constituent of many skeletal remains found in marine sediments. Further, calcium concentration is important in understanding carbonate concentration in the sea. Potassium is the fourth abundant cation and is present as 4 per cent of the concentration of sodium. One cubic meter (35.3165 cu.feet) of sea water contains about 28 to 31 kilos of sodium chloride and 5 to 6 kilos of potassium chloride.

C) Progress of evaporation of seawater

Nature has ~~gifted~~ given India with the most favourable climatic conditions for the large scale manufacture of quality salt from sea-brine by solar evaporation. High evaporation rate, high temperature, low rainfall, favourable wind velocity and longer duration of hot season are the important factors which have favoured India for the manufacture of salt from sea brine by solar evaporation. These climatic conditions are also favourable for the manufacture of by-products by evaporation followed by fractional crystallisation for obtaining higher density bitterns by a process of eliminating the various salts. By solar evaporation, it is possible to obtain a mixed salt fraction rich in potassium chloride, magnesium sulphate and sodium chloride from the bitterns, which forms the raw material for the establishment of marine chemical industries complex at various places in India, especially in Gujarat. Utilising these favourable conditions, India produces nearly four million tonnes of common salt per year by solar evaporation of sea water. About 24,000 tonnes of calcium carbonate and 2.3 lakh tonnes of gypsum ($CaSO_4 2H_2O$) are precipitated out during the course of evaporation of sea water. The bittern left after the harvest of common salt contains about 4.6 lakh tonnes of unrecovered sodium chloride, 2.3 lakh tonnes of epsom salt, one lakh tonnes of potassium chloride, 6 lakh tonnes of magnesium chloride and nearly 9200 tonnes of bromine. The above chemicals which are now going waste, except for small recovery at two or three salt works are of considerable economic value and are worth recovering for their demand in the country for a wide variety of uses.

Among the main by-products from salt works is gypsum, which is used in the manufacture of fertilisers, portland cement as a plaster material and in paint industry as filler. Gypsum has also attained importance as a raw material for the manufacture of sulphuric acid. Gypsum ($CaSO_4 \cdot 2H_2O$ or anhydri~~d~~te $CaSO_4$) is used as a source of sulphur dioxide. Instead of lime stone in cement kiln, a mixture of gypsum, clay and ground coke is charged into the rotary kiln. The partial reaction is $CaSO_4 + C = CaO + SO_2 + CO$. The carbon monoxide is converted to carbon dioxide and lime is combined with clay to form cement. The exit gases contain 6 to 7 per cent sulphur dioxide. This is used in a standard contact process to form sulphuric acid. Therefore, the recovery of gypsum from all the salt producing centres in India has become a dire necessity.

Potassium chloride is the second important by-product that can be obtained from the salt works. It is required in large quantities for the manufacture of potassium chlorate and potassium dichromate. It is used extensively as fertiliser. The only important and perennial source for the manufacture of potassium chloride is bittern from marine salts industry. About 40,000 tonnes of potassium chloride can be manufactured annually on the basis of practical recovery on the present production of common salt in the country. The potential demand of this chemical by end of 1970 is estimated as 2.5 lakh tonnes.

The third important chemical in series is magnesium chloride which is used for sizing in the textile industry and for the preparation of magnesia cement. Another product that can be recovered is magnesium sulphate which is used in tanning and dyeing industries, in the manufacture of paints and in the finishing of cotton goods. It is also used for wetting paper, silk and leather. Bromine is the fourth by-product from the salt industry which is used in organic synthesis and its compounds find application in photography and in the manufacture of sedative drugs, dyes and anti-knock compounds.

Therefore, the various processes including the principle and technology for the recovery of these by-products from salt works are described.

Before going with the process or technology of individual by-products, it may be worthwhile to know the different salts that will be separating at different stages in the concentration of sea brine and what stages one has to look after for the recovery of these by-products.

Ist stage (3.5 to 10° Be)

By evaporating the brine of 3.5° Be until it attains a density of 10° Be, the original volume is reduced to 37 per cent. At this stage, most of the calcium carbonate is thrown out. Calcium carbonate is abundantly available in India and its recovery from brine is of no economic value.

IInd stage (10° to 17° Be)

At 17° Be the volume of brine is reduced to 20 per cent of the original. Small quantities of calcium sulphate and all the remaining calcium carbonate separate out at this stage. Since this fraction is a mixture of $CaCO_3$ and $CaSO_4$ it is of no value.

IIIrd stage (17 to 24.5° Be)

Calcium sulphate separates out as gypsum ($CaSO_4 2H_2O$) at this stage. For good recovery of gypsum, the last condensor in the series employed for the concentration of brine from 17 to 24° Be, is to be used for the recovery of gypsum. The good practice followed in salt works is that the bed of the condensor is tampered at the beginning of the season, drained off completely at the end of the season and the bed is allowed to dry up for 3 - 4 days. Crude gypsum detaches itself from the bed in the form of crust and is r~~e~~acked out. It is then washed by rain and dried on bamboo mats or suitable mats to give a product containing not less than 97 per cent gypsum. It is estimated that for every 100 tonnes of salt produced 5 to 6 tonnes ($CaSO_4 2H_2O$) of gypsum can be obtained based on the practical recovery of 60 per cent.

IVth stage (24.5 to 29° Be)

The crystallisers are fed with brine of 24° Be. The density of saturated solution of pure sodium chloride is 26° Be. However, if other salts are present in solution the mixed solution especially with magnesium chloride behaves as if it is saturated with respect to salt at

24.5° Be. The density remains between 25 - 26° Be and begins to rise appreciably only after more than 50 per cent of salt separates out. As the density rises, more and more salt is thrown out until the brine attains a density 28.5 - 29° Be. At this stage, the brine is drained off and the salt is washed with 24° Be to remove adhering impurities. Only 70 - 75 per cent of the salt present in the brine, and not the entire amount separates out at this stage. 25 to 30 per cent sodium chloride is carried away into the bittern. The residual salt continues to separate out as the brine is concentrated upto 36° Be and beyond. Now the liquor is saturated with all marine salts and sodium chloride separates with other salts that is, the salt will be contaminated with magnesium sulphate, potassium chloride and magnesium chloride. The liquor after the recovery of common salt is termed as "bittern". Further concentration of bittern results in crystallisation of various salts at ~~various salts at~~ various stages of concentration as indicated below.

<u>Vth stage</u> (29/30° Be to 32° Be)

Crude salt separates which when washed with 24° Be liquor, yields good quality of salt (8 tonnes per 100 tonnes of salt produced).

<u>VIth stage</u> (32° to 34° Be)

Crude second grade salt below 80 per cent sodium chloride containing impurities like $CaSO_4$, $MgSO_4$, $MgCl_2$

(approximately 6 - 8 tonnes of crude salt, 80 per cent sodium chloride per 100 tonnes of salt produced) are obtained. At this stage, bromine can be recovered from bittern by treatment with chlorine as bromine content in bittern is maximum at this concentration. It contains about 18 g of bromine per litre.

VIIth stage (34° to 36° Be)

Solid separates out rich in magnesium sulphate. Average composition will be 45-50 per cent sodium chloride and 24 to 28 per cent magnesium sulphate. This fraction is known as "Sel's Mixts" and can be used directly for the precipitation of magnesium sulphate and sodium sulphate by chilling process.

VIIIth stage (36° to 38° Be)

Salt mixture containing potassium chloride, sodium chloride, magnesium sulphate and magnesium chloride is obtained during this stage of evaporation of bittern. This fraction can be used for the recovery of potassium chloride and magnesium sulphate. The average composition of the fraction is KCl 18-20 per cent, NaCl 18 to 20 per cent, $MgSO_4$ 30 to 35 per cent and $MgCl_2$ 6 to 8 per cent. For every 100 tonnes of salt produced, 6 to 6.5 tonnes of mixed salt can be harvested.

IXth stage (38° Be)

The liquor contains mainly magnesium chloride. It can be used for the preparation of fused magnesium chloride ($MgCl_26H_2O$), magnesium carbonate and anhydrous magnesium chloride for magnesium metal industry. This liquor contains a small amount of NaCl and KCl to the extent of 1.5 per cent and magnesium sulphate 4 to 5 per cent. The concentration of $MgCl_2$ is about 30 per cent (35 per cent w/v). For every 100 tonnes of salt produced we can obtain 17.6 tonnes of $MgCl_2 6H_2O$ calculated on the practical recovery of 60 per cent (Table 2).

Recovery of various salts from sea water is based on classical equilibrium studies[1] of ternary, quaternary and reciprocal salt pair systems by Van't Hoff; Meyerhoffer and as reviewed by E. Janecke[2], J.D. Ans[3], Lowenherz and others. Force evaporation studies are reported by J.H. Hildebrand[4], while isothermal evaporation and metastable equilibrium conditions are reported by I.N. Lepeshkov, N.V. Bodaleva[5], H. Autenrieth[6] and J.D. Ans.[3]

Solar evaporation of bitterns and deposition of mixed salts is reported by Regnault[7] and Niccoli. R. who carried out evaporation of sea water under density control conditions between 1.31 to 1.35. In absence of any knowledge of its chemical composition, Niccoli called the evaporites ~~as~~ mellachite an Aribic name from the name of a place (Mellache) situated on the eastern coast of Africa. Systematic study and separation of mixed salt rich in potassium chloride from sea bittern are not thoroughly examined by workers and the production and its utilisation as a potash basic raw material has remained ~~as~~ obscure in literature. The evaporation of bitterns for the production of mixed salt forms a part of the thesis and is reported in detail in Section II.

Table 2 Stages in evaporation of sea water

No.	Stage	Major separated salt	Volume reduction (per cent)	Condition of liquor
1	3.5°Be to 10.0°Be	$CaCO_3$	37	saturated with $CaCO_3$
2	10.0°Be to 17.0°Be	$CaCO_3$	20.0	-do- and $CaSO_4$
3	17.0°Be to 24.5°Be	$CaSO_4 2H_2O$	12.5	saturated with $CaSO_4$
4	24.5°Be to 29° Be	NaCl	2	saturated with NaCl
		Bittern evaporation		
5	29° Be to 32° Be	NaCl	1.50	saturated with $MgSO_4$
6	32°Be to 33° Be	NaCl $MgSO_4 7H_2O$	1.40	"
7	33° to 34° Be	"	1.26	"
8	34°to 35° Be	NaCl,$MgSO_4 6H_2O$	1.14	"
9	35° to 36°Be	NaCl,$MgSO_4 6H_2O$	1.02	saturated with KCl
10	36° to 38° Be	KCl, $MgSO_4 6H_2O$ (NaCl)	0.86	"
11	38° Be to solidification	$MgCl_2 6H_2O$	-	saturated with $MgCl_2$

The technique behind it to isolate the chemicals by fractional crystallisation is dealt with in the branch of chemistry known as" phase rule". The process of fractional crystallisation is very valuable for the recovery of various salts from bittern and it is thoroughly studied from the stand point of application of phase rule. The phase rule defines the relationship between the components, number of phases and degrees of freedom for heterogeneous equilibrium system by simple expression, as $P + F = C + 2$; where P is defined as number of phases which is distinctly physical constituent out of the component and the component is defined as an independent chemical composition which constitutes the phases. The degrees of freedom are defined as temperature, pressure and concentration. In a simple language if temperature is changed the composition will also change. In an equilibrium state the number of phases are fixed. For aqueous system, pressure does not alter much and hence it is less important in the process technology. Temperature and concentrations are most important for the separation of salts. At first it is necessary to investigate the equilibrium conditions and phase relation of the system in question. The solubility data are represented on a suitable chart and diagram from which one can predict what changes will take place in the system on bringing about any given variations in the conditions. The diagram will also show what salts will crystallise out from the solution of any given concentration on evaporation or cooling to any given extent and one can also be able to calculate the quantities which will separate. The application of the above principle with diagrams in detail are dealt with appropriately in various chapters of this thesis.

Applications of the phase rule and solubility diagrams in various salt based chemical industries are briefly described for the clear understanding.

(1) NaCl - H_2O system: The solubility curve with temperature is a straight line and is not steep. Hence sodium chloride cannot be separated out by chilling but only by evaporation. Only one solid phase exists, NaCl (Table 3; Fig. 1).

(2) Na_2SO_4 - H_2O system : The solubility curve is very steep and sodium sulphate can be recovered by chilling. It exists in two solid phases Na_2SO_4 and $Na_2SO_4 10H_2O$. The diagram indicates that Na_2SO_4 separates with decahydrate below 32.5° C. To obtain anhydrous salt it is necessary to raise temperature above 32.5° C. (Table 4; Fig. 2). System Na_2SO_4 - NaCl - H_2O (Table 5; Fig. 3) show that by addition of sodium chloride, the transition temperature is lowered to 17.5° C. Solubility of sodium sulphate is depressed. This property is made use of in the dehydration of sodium sulphate as reported in section II, chapter 2 of this thesis.

(3) NaCl - KCl - H_2O system: The phase diagrams are slightly complicated with mixtures like NaCl - KCl. The diagram is useful for purification of impure potassium chloride and forms a guide for the separation of potassium

chloride from NaCl + KCl mixture. By heating and cooling to room temperature, 11 grams of potassium chloride can be separated out for every 100 grams of solution (Table 6; Fig. 4,5).

(4) KCl - $MgCl_2$ - H_2O system: The system is used for decomposition of carnallite with water to obtain impure potassium chloride. The diagram contains two invariant points (1) KCl + carnallite (2) Carnallite + $MgCl_2$ with three solid phases KCl, $MgCl_2$, $KCl.MgCl_26H_2O$. If one desires to have only potassium chloride from carnallite one has to add the calculated quantity of water to equate with the composition of first invariant point. Generally one part of solid carnallite with half the quantity of water will give impure potassium chloride without magnesium chloride. In order to calculate the amount of NaCl that is expected to separate as impurity, one has to consider the quaternary system NaCl - KCl - $MgCl_2$ - H_2O. Magnesium chloride suppresses the solubility of sodium chloride and is thrown out along with potassium chloride (Table 7, 8; Fig. 6,7).

Another most complicated system in phase rule is reciprocal salt pair system. The important example is the manufacture of sodium carbonate by Solvey ammonia process. The reaction can be represented as

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2 \text{ (Calcination at 800°C)}$$

This represents two salt pairs having no common ion. $NaHCO_3$ and NH_4Cl is stable solid phase when NaCl is reacted with NH_4HCO_3 being less soluble precipitates out as salt ~~figure~~ 8 (Table 9, Fig. 8).

5) $NaCl - KCl - MgCl_2 - MgSO_4 - Na_2SO_4 - H_2O$ system:

The above quinary systems at 25° and 83°C are represented in (Table 10, 11; Fig. 9 & 10) Van't Hoff has studied the above classical systems connected with the oceanic salt deposits and a glance at these two diagrams indicate that solid phases at 25°C and 83°C are different. The bischofite, carnallite, sylvite, glaserite and thenardite are present at both the temperatures. The disappearance of $MgSO_4 6H_2O$, kainite, epsom salt, leonite, schoenite, astrakanite and appearances of kieserite, langbeinite, lowite, vanthoffite at higher temperature are prominent. To understand the scientific basis of various developed processes reported in this thesis, these diagrams are very helpful and reported appropriately in detail in various chapters. Thus application of solubility data on oceanic salts has been utilised to evolve two novel processes for preparation of mixed salt and its utilisation for (1) the manufacture of potassium chloride, magnesium sulphate and sodium sulphate and 2) obtaining potash alum.

Salt producing centres and composition of brines

The principal salt producing centres in India are a) marine salt works in Bombay, Kathiawad, Kutch, Madras, Orissa and Travancore b) inland sources of Rajastan, Kharaghoda, Dhrangadhra c) the rock salt mines in Mandi (Himachal Pradesh).

Table 3 Solubility data of the system NaCl - H_2O

t	d	g NaCl per 100 g Sat.soln	g NaCl per 1000 g H_2O	Solid phase
- 21.1	-	23.0	298.6	Ice + $NaCl2H_2O$
- 15	-	24.3	320.2	$NaCl2H_2O$
- 10	-	25.0	333.3	"
- 5	-	25.6	344.1	"
+ 0.1	-	26.3	356.0	" + NaCl
+ 10.0	-	26.4	357.0	NaCl
20.0	1.2001	26.5	358.0	"
30	-	26.6	360.0	"
40	-	26.7	363.0	"
60	-	27.1	371.0	"
80	-	27.6	380.0	"
100	-	28.3	391.0	"

E at - 21.1°C Eutectic, Cryohydric or freezing point of solution.

U at + 0.015°C Transition point between NaCl and $NaCl.2H_2O$

P at + 108.7°C Boiling point at 760 mm.

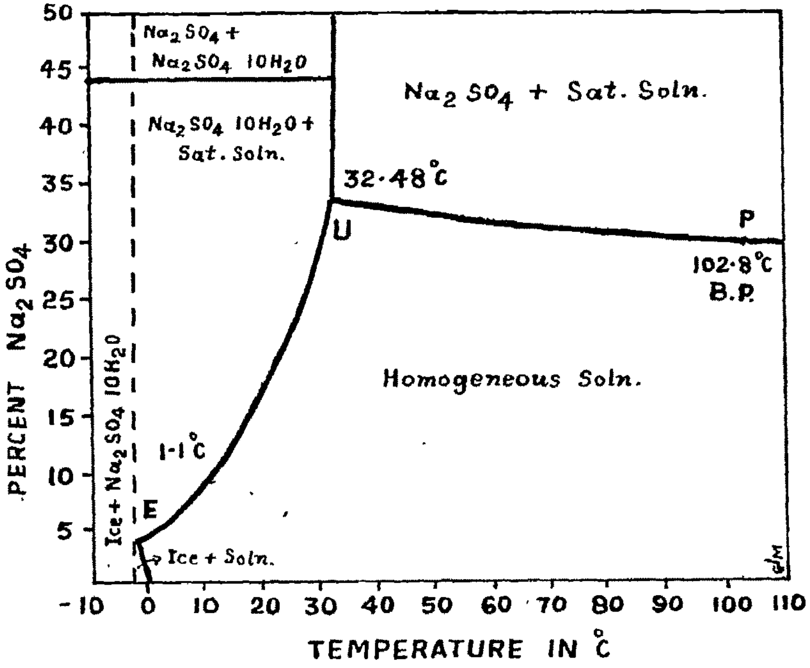


Fig. 2 System $Na_2SO_4 - H_2O$

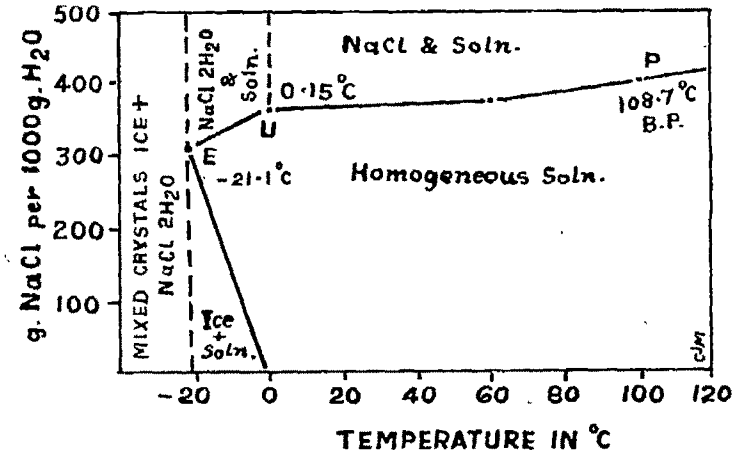


Fig. 1 System $NaCl - H_2O$

Table 4 Solubility data of the system Na_2SO_4

t°C	d	g Na_2SO_4 per 100 g H_2O	Solid Phase
0.70	1.0432	4.71	Na_2SO_4-$10H_2O$
10.25	1.0802	9.21	"
15.65	1.1150	14.07	"
20.35	1.1546		
24.90	1.2067	27.67	
27.65	1.2459	34.05	
30.20	1.2894	41.78	
31.95	1.3230	47.98	
32.5	tr. pt.		$Na_2SO_4 10H_2O$ + Na_2SO_4
33.5	1.3307	49.39	Na_2SO_4
38.15	1.3229	48.47	"
44.85	1.3136	47.49	"
60.10	1.2918	45.22	"
75.05	1.2728	43.59	"
89.85	1.2571	42.67	"
101.9(B.P)	1.2450	42.18	"

E at -1.10°C Eutetic, cryohydric, or freezing point of solution

U at 32-48°C Transition temperature (S_{10}, S, Soln.)

P at 102.8°C Boiling point at 760 mm.

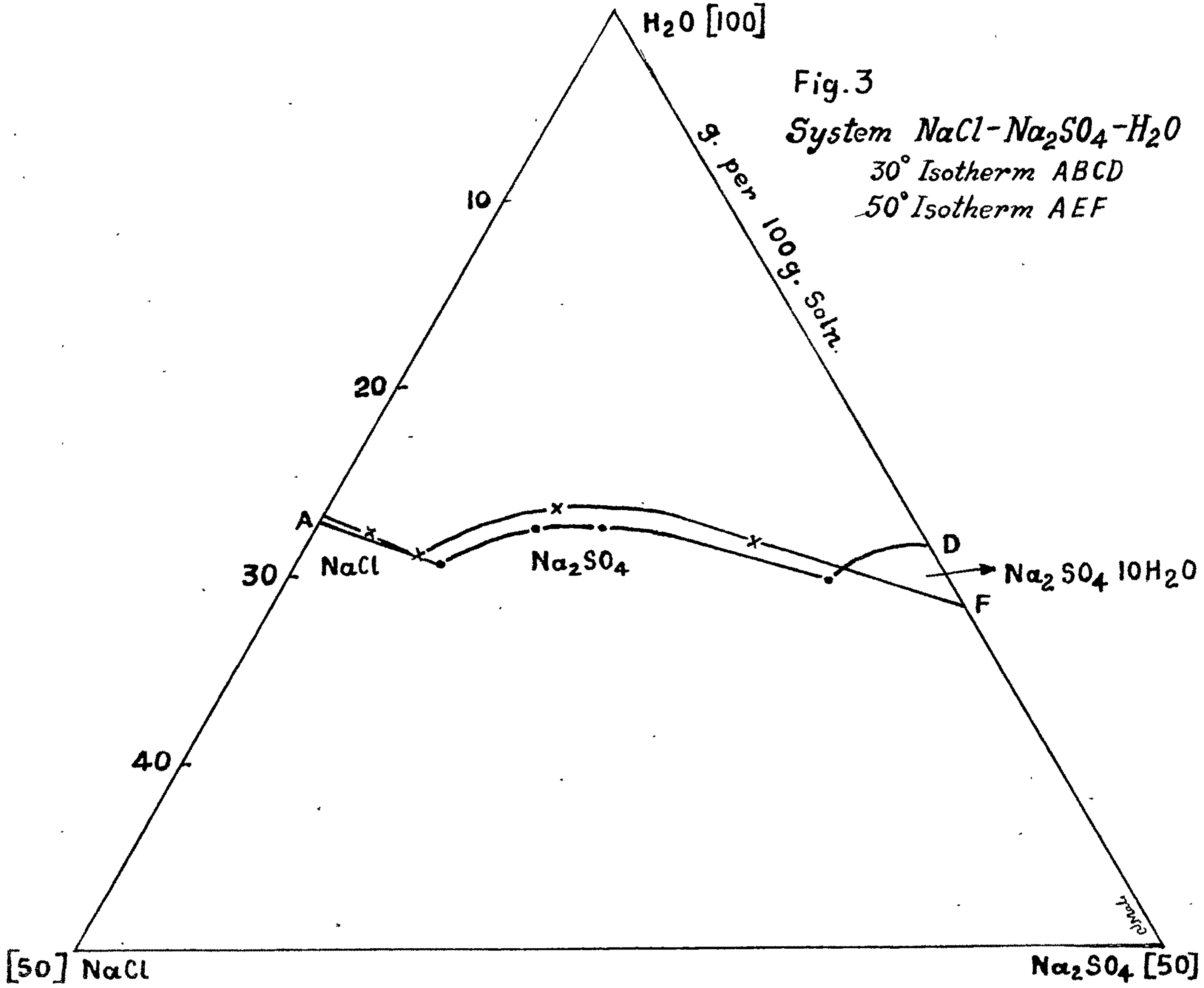


Fig. 3

System $NaCl-Na_2SO_4-H_2O$

30° Isotherm ABCD

50° Isotherm AEF

Table 5 Solubility data of the system NaCl - Na_2SO_4-H_2O at 30°C Isotherms

(g per 100 g water)

Sp.Gr. of soln.	NaCl	Na_2SO_4	Total solids	NaCl/Na_2SO_4
1.281	0.00	39.70	39.70	-
1.282	2.45	38.25	40.70	0.06
1.284	5.61	36.50	42.11	0.15
1.290	7.91	35.96	43.87	0.22
1.275	10.61	31.64	42.25	0.33
1.270	12.36	29.87	42.23	0.41
1.258	15.65	25.02	40.67	0.62
1.249	18.44	21.30	39.74	0.86
1.244	20.66	19.06	39.72	1.08
1.236	32.43	9.06	41.49	3.58
1.200	36.03	0.00	36.03	-

Transition point of $Na_2SO_4 . 10H_2O$ (32.5) is lowered to 17.5°C in presence of NaCl.

Fig. 4 System $NaCl-KCl-H_2O$

SPACE MODEL

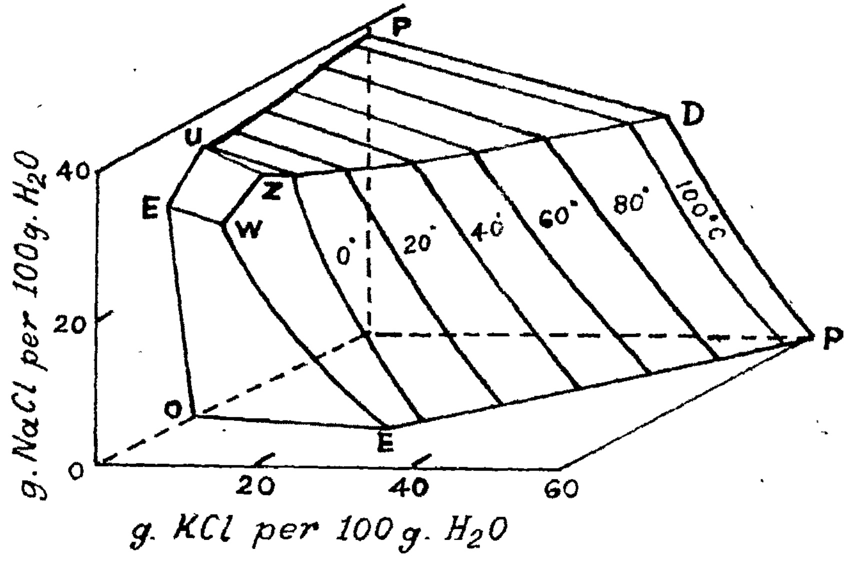


Fig. 5 System $NaCl-KCl-H_2O$ at 20°C isotherm and B.P. isobar

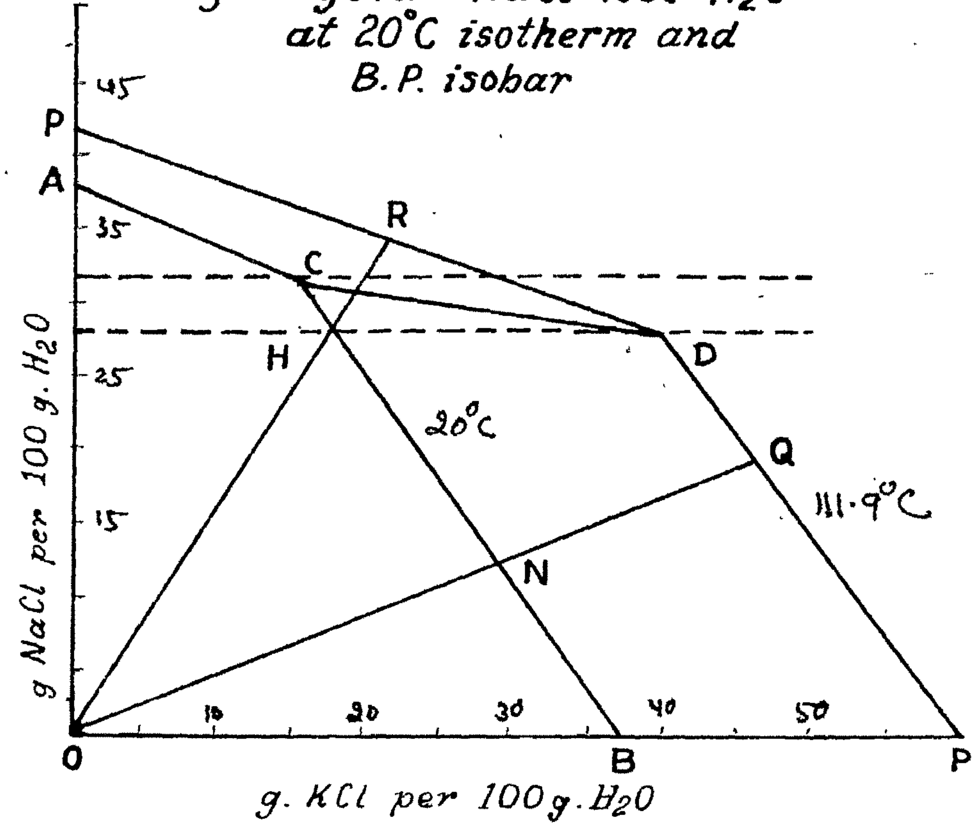


Table 6 Solubility data of the system KCl - NaCl - H_2O

(g per 100 g H_2O)

	Cryohydric and transition points			
Point	Temp.C	KCl	NaCl	Solid phases
W	- 22.9	7.8	27.3	Ice+KCl+$NaCl.2H_2O$
E	- 21.1	-	30.0	Ice+$NaCl.2H_2O$
E'	- 10.7	24.3	-	Ice+KCl
Z	- 2.3	9.9	32.0	KCl+NaCl+$NaCl.2H_2O$
U	+ 0.1	-	35.6	NaCl + $NaCl.2H_2O$

Solubility isotherms			Invariant points	
			KCl	NaCl
0	28.1	35.6	10.3	31.8
20	34.3	35.8	14.8	30.4
40	40.2	36.3	19.6	29.3
60	45.5	37.0	24.6	28.4
80	50.6	37.9	30.0	27.7
100	55.5	38.9	35.3	27.5

	Boiling points			Invariant points	
P^1	108.5	57.6	-		
P'	118.7	-	39.4		
D	111.9	-	-	38.6	27.5

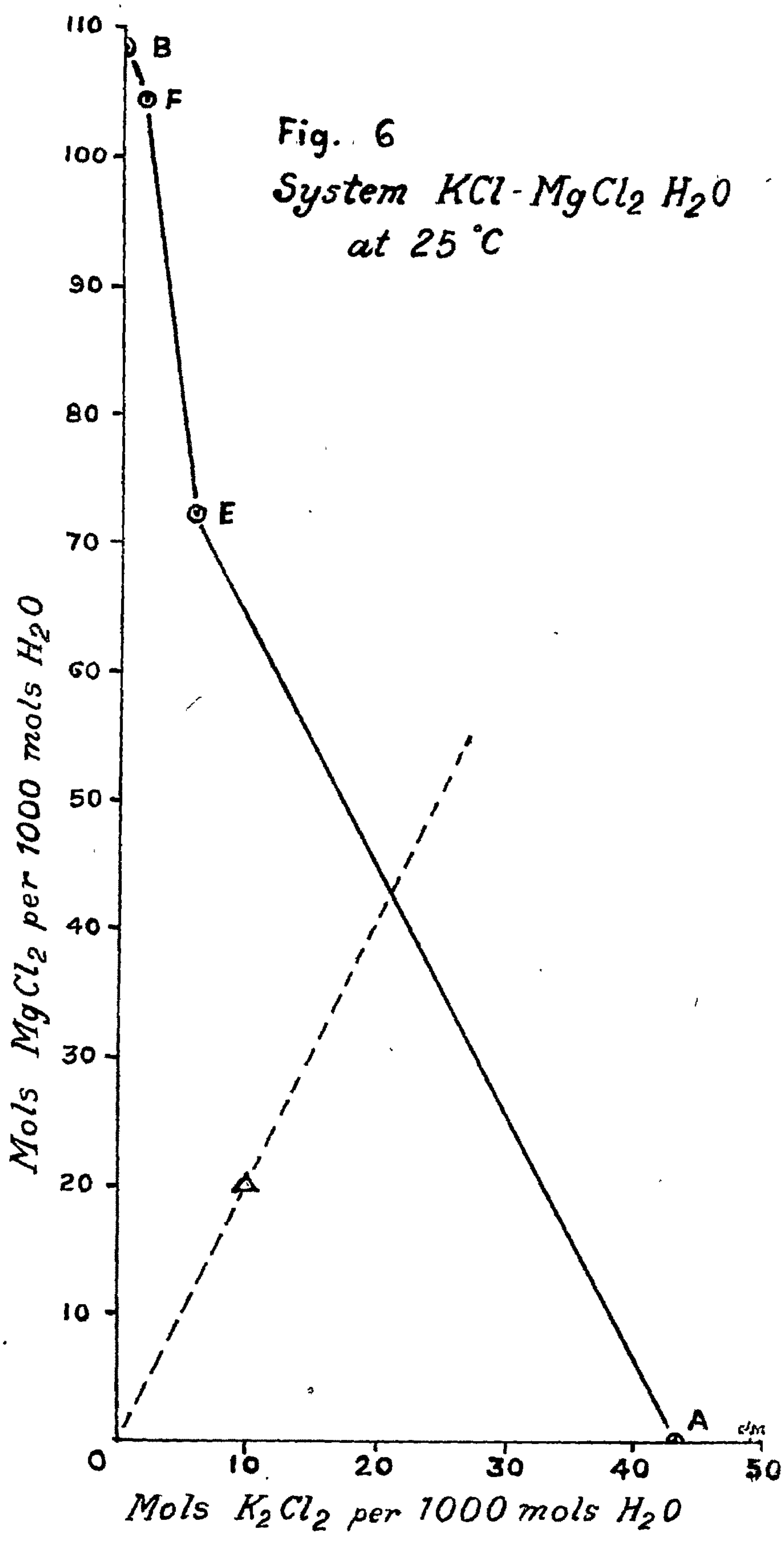


Fig. 6
System $KCl-MgCl_2\ H_2O$
at 25 °C

Table 7 Solubility data of the system $KCl-MgCl_2-H_2O$ at 25°C

		Per cent		Moles per 1000 moles of water	
Point	Solid phases	KCl	$MgCl_2$	K_2Cl_2	$MgCl_2$
A	KCl	26.52	-	44	-
B	$MgCl_2.6H_2O$	-	35.65	-	108
E	KCl-carnallite	3.48	26.6	5.5	72.5
F	$MgCl_2.6H_2O$ carnallite	0.54	29.9	1	105

If decomposition is carried out at E 7.5 per cent KCl remains in solution and 92.5 per cent is obtained as solid.

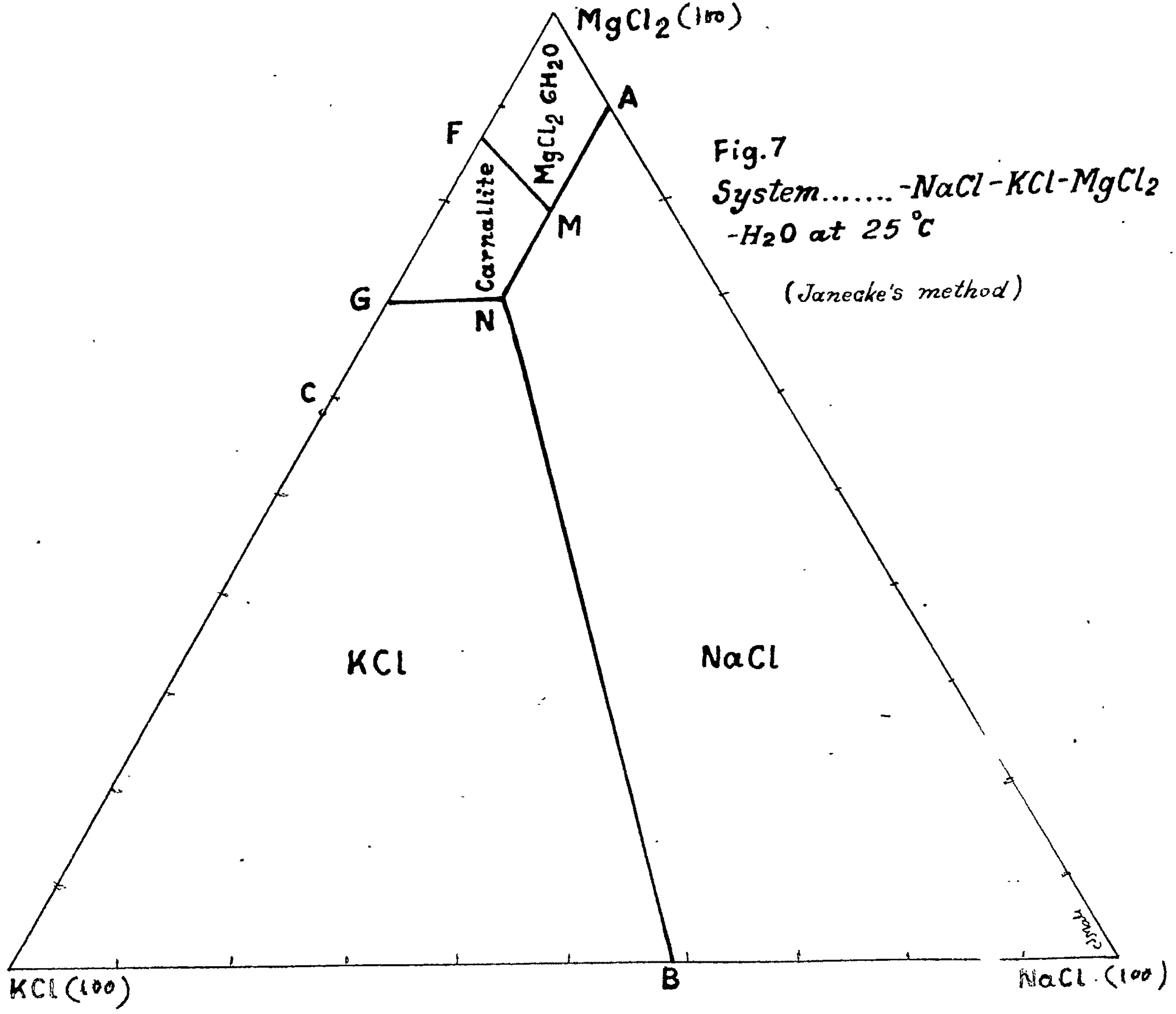


Fig.7
System.......-NaCl-KCl-MgCl$_2$ -H$_2$O at 25 °C

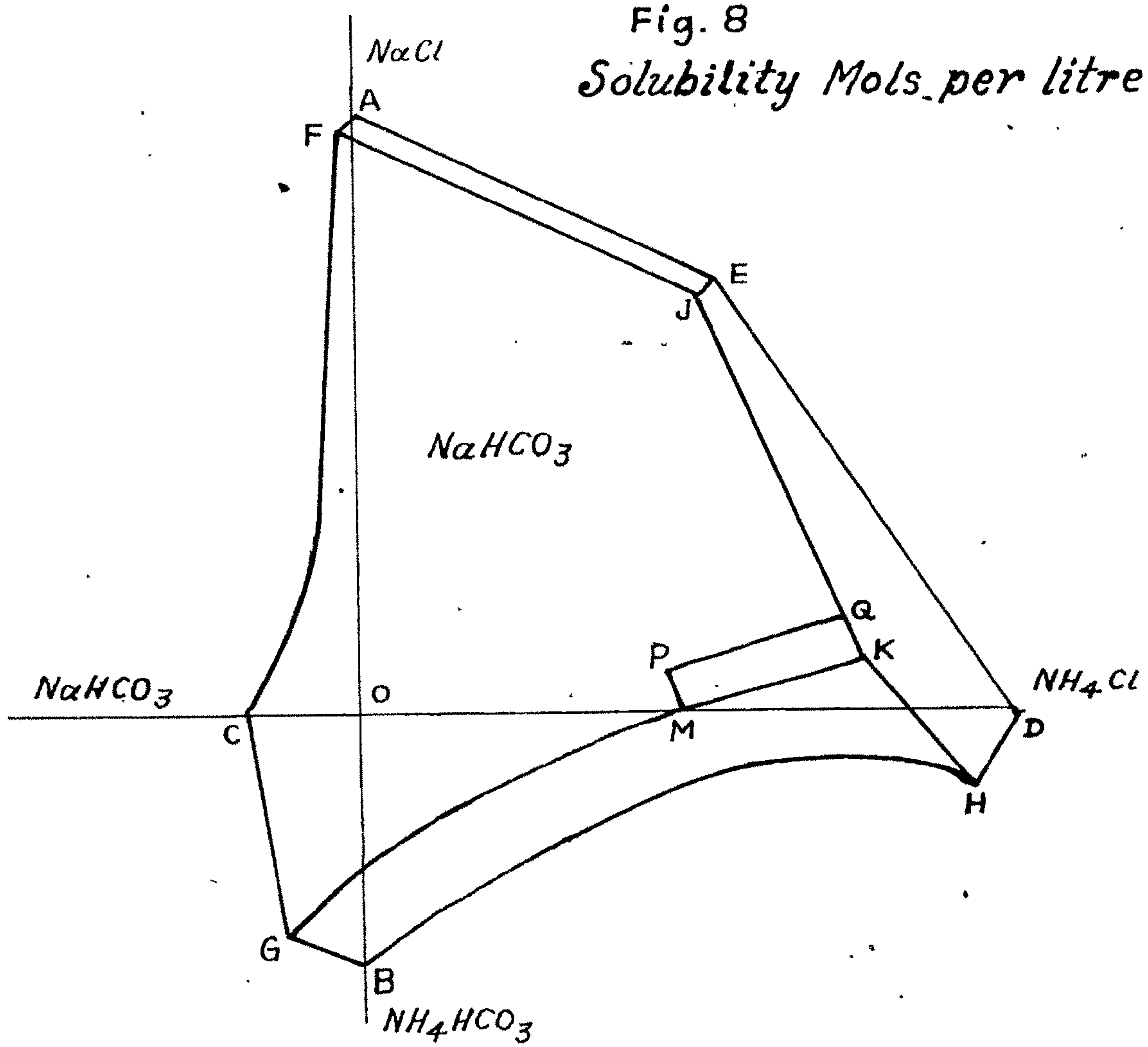
(Janecke's method)

Table 8 Solubility data of the system KCl-NaCl-$MgCl_2H_2O$ at 25°C.

	Per cent			
Sp.gr	NaCl	KCl	$MgCl_2$	Total salts
1.234	20.42	19.14	-	31.56
1.244	6.87	6.39	15.87	29.13
1.262	2.81	4.17	23.02	30.00
1.276	2.36	3.29	25.54	31.19
1.270	-	3.49	26.78	30.27
1.280	1.50	0.91	27.54	30.95
1.337	0.32	0.12	35.56	36.00
1.337	0.34	-	35.44	35.78
1.337	-	0.12	35.56	35.68

Fig. 8

Solubility Mols per litre of water

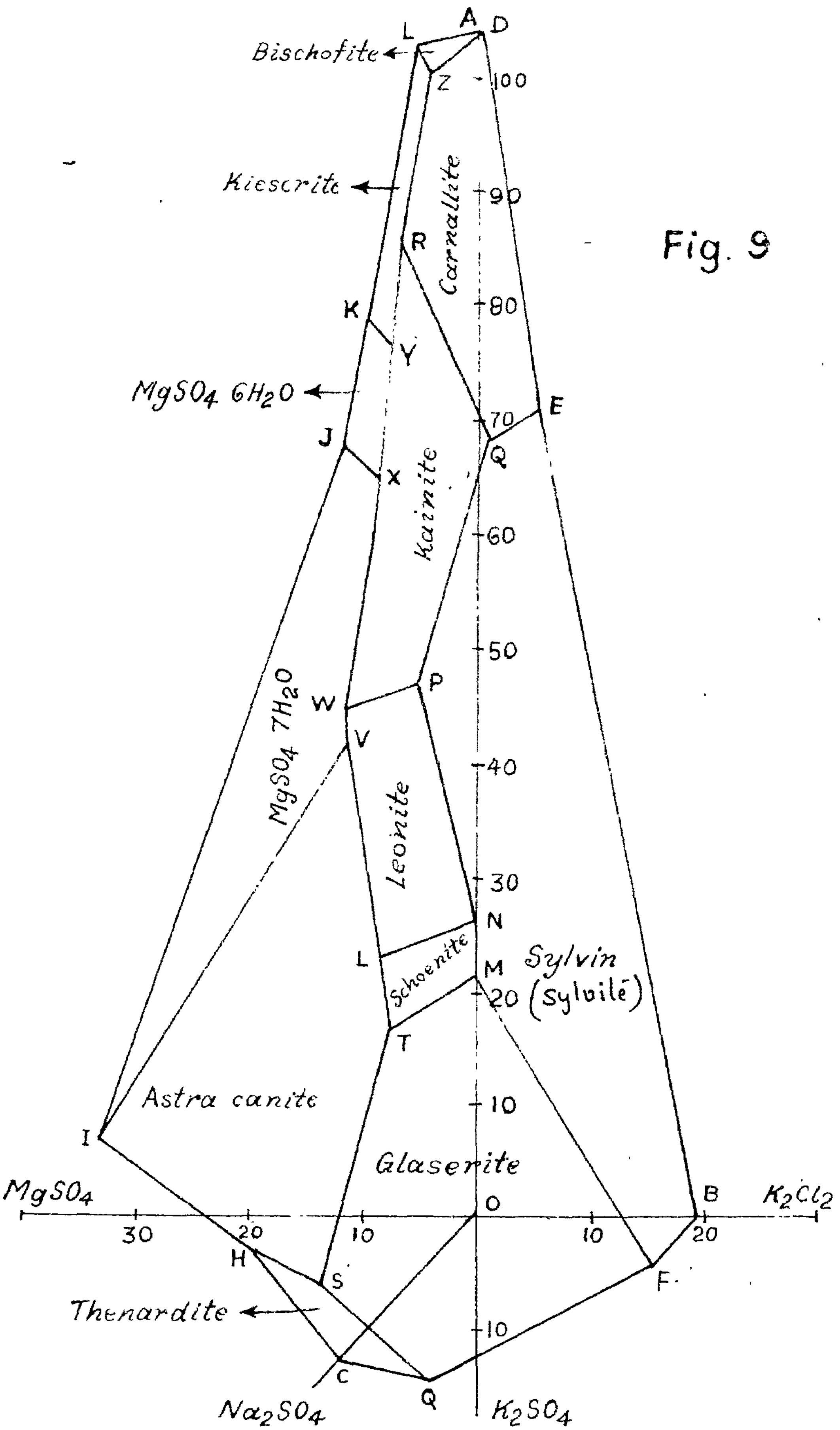


$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 + NH_4Cl$ - 15°C

Table 9 Solubility data of the system NaCl + NH_4HCO_3 = $NaHCO_3$ + NH_4Cl at 15° C

Temp.	NaCl	NH_4HCO_3 =	K_1	$NaHCO_3$	NH_4Cl =	K_2	K_1/K_2
0	6.09	1.51	9.2	0.82	5.50	4.52	2.03
10	6.10	2.00	12.2	0.97	6.23	6.05	2.03
15	6.11	2.32	14.2	1.07	6.58	7.07	2.01
20	6.13	2.66	16.3	1.14	6.95	7.94	2.05

Fig. 9



System $NaCl$-KCl-$MgCl_2$-$MgSO_4$-Na_2SO_4-H_2O at 25 °C

MgSO$_4$ -H$_2$O

Table 10 Solubility data of the system NaCl-KCl-MgCl$_2$-Na$_2$SO$_4$ at 25°C
(Mols per 1000 mols H_2O)

Pt.	Solutions saturated with NaCl	2NaCl	2KCl	$MgCl_2$	$MgSO_4$	Na_2SO_4
O	(NaCl)	55.5	-	-	-	-
A	$MgCl_2.6H_2O$ ...	1	-	106	-	-
B	KCl ...	44.5	17.5	-	-	-
C	Na_2SO_4 ...	51	-	-	-	12.5
D	$MgCl_2 6H_2O$, carnallite ...	1	0.5	105	-	-
E	KCl - carnallite ...	2	5.5	70.5	-	-
F	KCl - glaserite ...	44	20	-	-	4.5
G	Na_2SO_4 - glaserite ...	44	10.5	-	-	14.5
H	Na_2SO_4, astrakanite ...	46	-	-	16.5	3.0
I	$MgSO_4.7H_2O$, astrakanite ...	26	-	7	34	-
J	$MgSO_4.7H_2O$, $MgSO_4.6H_2O$ ...	4	-	67.5	12	-
K	$MgSO_4.6H_2O$, kieserite ...	2.5	-	79	9.5	-
L	Kieserite, $MgCl_2 6H_2O$ ...	1	-	1.1	5	-
M	KCl, glaserite, schoenite ...	23	14	21.5	14	-
N	KCl, schoenite, leonite ...	19.5	14.5	25.5	14.5	-
P	KCl, leonite - kainite ...	9.5	9.5	47	14.5	-
Q	KCl, kainite - carnallite ...	2.5	6	68	5	-
R	Carnallite, kainite, kieserite ...	1	1	85.5	8	-
S	Na_2SO_4, glaserite, astrakanite ...	42	8	-	16	6
T	Glaserite, astrakanite, schoenite..	27.5	10.5	16.5	18.5	-
U	Leonite, astrakanite, schoenite ..	22	10.5	23	19	-
V	Leonite, astrakanite, $MgSO_4.7H_2O$ ..	10.5	7.5	42	19	-
W	Leonite, kainite, $MgSO_4.7H_2O$ ...	9	7.5	45	19.5	-
X	$MgSO_4.6H_2O$, Kainite, $MgSO_4.7H_2O$ ..	3.5	4	65.5	13	-
Y	$MgSO_4.6H_2O$, kainite, $MgSO_4.7H_2O$	1.5	2	77	10	-
Z	Carnallite, $MgCl_2.6H_2O$, kieserite	1	0.5	100	5	-

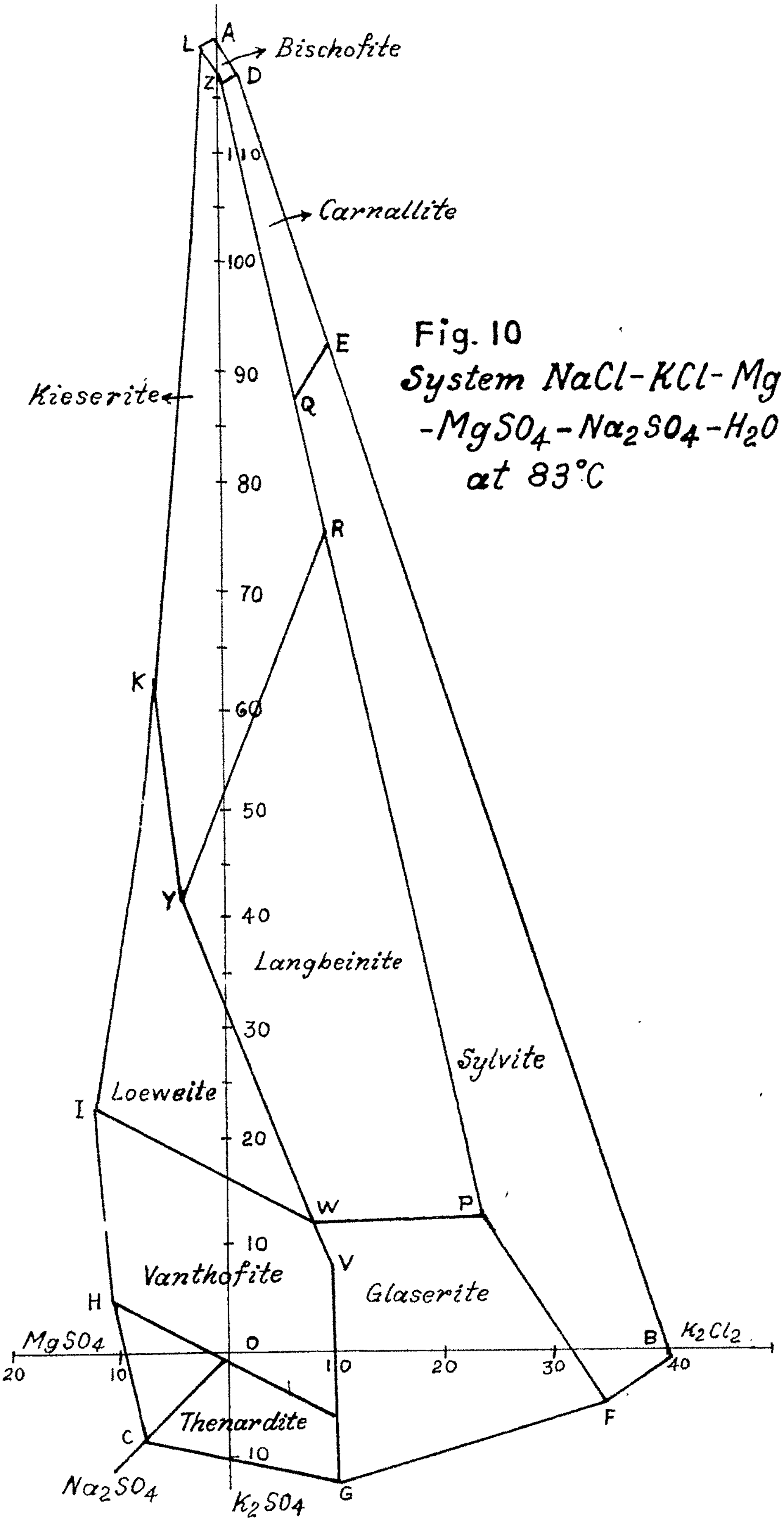


Fig. 10

System $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4-H_2O$ at 83°C

Table 11 Solubility data of the system NaCl -KCl - $MgCl_2$- $MgSO_4$-Na_2SO_4 - H_2O at 83°C. (Mols per 1000 mols H_2O)

Pt.	Saturated with NaCl and		Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Na_2SO_4
O		...	59	-	-	-	-
A	$MgCl_2.6H_2O$	...	1	-	121	-	-
B	KCl	...	39	37	-	-	-
C	Na_2SO_4	...	56.5	-	-	-	8
D	$MgCl_2.6H_2O$ + carnallite	...	1	2	117	-	-
E	KCl + carnallite	...	1.5	10	92	-	-
F	KCl + glaserite	...	39.5	39	-	-	4.5
G	Na_2SO_4 + glaserite	...	43.5	21	-	-	11.5
H	Na_2SO_4 + vanthoffite	...	51	-	4.5	10.5	-
I	Vanthoffite + loeweite	...	35	-	22	12.5	-
K	Loeweite + kieserite	...	12.5	-	61.5	5.5	-
L	Kieserite + $MgCl_2.6H_2O$	...	1	-	120	1	-
P	KCl, glaserite, langbeinite	...	29.5	33.5	13	10	-
Q	KCl, carnallite + kieserite	...	2	12	86.5	5	-
R	KCl, langbeinite + kieserite	...	11	15	76	5	-
S	Glaserite, Na_2SO_4, vanthoffite	...	43	22.5	-	7.5	5.5
V	Loeweite, glaserite, vanthoffite	..	34.5	26.5	8.5	17.5	-
W	Loeweite, glaserite, langbeinite	...	30	24.5	12	16.5	-
Y	Loeweite, kieserite, langbeinite	..	16	10.5	42	14	-
Z	Carnallite, $MgCl_2.6H_2O$, kieserite	..	1	2	116	1	-

Mineralogical name	Formula	Mineralogical name	Formula
Bischofite	$MgCl_2.6H_2O$	Carnallite	$KMgCl_3.6H_2O$
Sylvin (sylvite)	KCl	Glaserite	$Na_2K_4(SO_4)_3$
Thenardite	Na_2SO_4	Astrakanite	$Na_2Mg(SO_4)_2.4H_2O$
Reichardtite	$MgSO_4.7H_2O$	Schoenite	$K_2MgSO_4)_2.6H_2O$
Kieserite	$MgSO_4.H_2O$	Leonite	$(K,Na)Mg(SO_4)_2.4H_2O$
Langbeinite	$Mg_2K_2(SO_4)_3$	Kainite	$KCl.MgSO_4.3H_2O$
Vanthoffite	$MgNa_6(SO_4)_4$	Loeweite	$Mg_2Na_4(SO_4)_4.5H_2O$

India occupies the fourth place among the salt producing countries of the world and has annual production of 6 million tonnes. Seventy per cent of the produced salt is from the sea, while the rest is produced from subsoil or lake brines and a meagre quantity from mines. The salt factories are well laid for solar evaporation. Temperature of air is usually 85 to 112° F and is fairly uniform throughout the year. The rainy days are in the months from June to September on the west coast, while it is September to January on the east coast.

In marine salt works, the brine is obtained from sea, whilst inland salt works it is either obtained from salt lakes or tapped from subsoils sources by means of shallow wells, pits and percolation chanals. Sea brine measures from 3 to 3.5° Be, whilst the subsoil brine varies from 3 to 19° Be. Even though copious subsoil brine is available the lifting of brine is only by manual labour as the time of recuperation is large. Compositions of subsoil brines are not constant as that of sea water. The compositions of the solids in the brines obtained in inland lakes and from wells are not only peculiar to locality but even in the same locality they vary from time to time and at different depths at the same time. The differences in composition between sea-lake and well brines at the different salt works in India are given in Table 12. The various stages in evaporation of sea water, volume reduction of the original solution and the nature of the solution at the end of the respective stages are given in Table 2.

Table 12 Composition of Indian Sea, Lake and Well brines

(per cent on dry basis)

Constituents	seawater	lake brine Sambhar (Rajasthan)	WELL BRINES				Pit brine Vedaranyam
			Kharaghoda Gujarat	Kuda Gujarat	Didwana. (Rajastan)	Panch badra	
Calcium carbonate	0.345	...	0.060	0.073	---	...	...
Calcium sulphate	3.600	...	2.120	1.961	...	2.970	6.18 $CaCl_2$
Sodium chloride	77.758	87.300	70.800	72.342	77.190	85.660	60.03
Sodium sulphate	...	8.650	...	...	20.650	...	...
Sodium carbonate	...	3.870	...	...	0.600	...	...
Sodium bicarbonate	...	...	...	...	1.560	...	...
Magnesium sulphate	4.737	...	2.313	2.320	...	9.440	11.01
Magnesium chloride	10.878	...	22.360	21.795	...	1.930	22.70
Magnesium bromide	0.217	0.051	0.347	0.259	...	...	...
Potassium chloride	2.465	0.129	2.000	1.250	...	...	...

Recent investigations carried out in this Institute regarding the survey and compositions of Kharaghoda, Dhrangadhra and in greater Runn of Kutch brines show that two types of brines are available in these areas; 1) brines containing little sulphate 2) brines containing negligible or no sulphate. On an average magnesium chloride and bromine concentrations are higher whilst the potassium chloride contents are lower than that in sea water brines of similar densities. The evaporation of these brines is subject to same physical principals as the evaporation of sea water, but because of their pecularities the technique of manufacture though similar to that employed in production of salt and mixed salt from sea water has to be adopted to local conditions with minor modifications. The low sulphate bittern mainly gives mixed salt which is crude carnallite with 0 to 5 per cent magnesium sulphate, whilst the high sulphate bittern gives mixed salt containing 5 to 25 per cent magnesium sulphate.

Processes for potassium chloride recoveries from sea water and bitterns - a review

Brief outlines of the known processes and the processes developed by the institute on the recovery of potassium chloride from the sea bittern are described.

There are no potash deposits in India and the only important and perennial source for the manufacture of potassium chloride is bittern from marine salt industry.

Bittern contains potassium chloride in low concentrations of 2 to 2.5 g per 100 ml; which cannot be isolated by solar evaporation since magnesium sulphate and sodium chloride interfere in the precipitation of potassium chloride at all concentrations. Recovery of other chemicals are linked with the potassium chemical recoveries so as to make the recoveries of potassium chemicals economically possible.

Descriptions of potash recoveries as adopted at Girad-en-Camargue at the mouth of Rhine have been described by Wurtz[9] and Lung[10]. The process consists of concentrating 27° Be brine by solar evaporation to 32½° Be, when crude salt separates. Further evaporation to 35° Be separates a mixture of sodium chloride and magnesium sulphate as sel's mixts which is worked up for Glauber's salt. The liquor of 35° Be is kept during winter in large deep tanks (above 12°C) when epsom salt separates. The end liquor 33°Be is further concentrated to 37° Be by artificial heat to obtain magnesium chloride between 37 to 40° Be. Both hot liquors are run at the same time to an iron mixing pan taking care to maintain an excess of magnesium chloride. The sel's mixt which separates is removed. The hot liquors on cooling gives carnallite which are further processed for potassium chloride.

J.H. Hildebrand[4] has proposed a process which consists of following steps (1)to evaporate sea bittern until boiling point becomes 120°C and density at hot is 1.35. Mixture of sodium chloride and magnesium sulphate obtained is worked up for epsom salt. (2) the mother liquor on cooling gives carnallite which is worked up for recovery of potassium chloride (3) the remaining solution containing magnesium chloride is worked up for bromine and bischofite ($MgCl_26H_2O$). A similar process is independently worked out and described by T.Nishimura[11].

Similar to Hildebrand process worked out in U.S.A. during war time, is adopted for winning potassium chloride by Tata Chemicals, Mithapur. They have modified the process so that simultanesouly bromine, potassium chloride, sodium chloride (vacuum salt), magnesium sulphate and fused magnesium chloride are recovered. Bittern of 29° Be from salt works is concentrated in salt pans to 34.5° Be and crude salt is recovered. The bittern of 34° Be is used for recovery of bromine. Bittern of 34° Be is acidified to pH 3 - 4 and heated to 60° C. The bittern is now sprayed from the top of the granite chlorinating towers kept at 60°C. Steam is introduced at the bottom and chlorine is introduced at part of the way up the tower, counter current to descending bitterns. The bromine thus released due to displacement by chlorine is condensed and taken to the purification system in the stone-ware vessels with coils. Most of the bromine is converted to sodium and potassium bromide of pharmaceutical grade.

Another part of bitterns of 34.5° Be is chilled to 10°C by cooling coils of large capacity refrigeration units. Here, 50 per cent of magnesium sulphate separates out as pure epsom salt and sulphate content in bittern is reduced to half (approximately 3 to 4 g $MgSO_4$ per 100 ml). This desulphation is effected by the refrigeration method and epsom salt is obtained as by product. After partial desulphation of bittern, the liquor is concentrated to 40° Be in triple effect evaporators. On hot settling of this liquor, potassium chloride has remained in solution and a part of still remaining sulphate separates as kieserite ($MgSO_4H_2O$) which is allowed to settle in the settlers. The overflow from the hot settlers is taken to continuous crystallisers for the separation of carnallite ($KClMgCl_26H_2O$). Carnallite is decomposed with water (1:0.5). The impure potassium chloride is recrystallised by NaCl-KCl solution to obtain (58 to 60 per cent K_2O) potassium chloride. The tail liquor from potassium chloride contains mostly magnesium chloride, collidal organic matter, a small quantity of magnesium sulphate and potassium chloride. The organic matter is destroyed by addition of oxidising agent ($KClO_3$), and lime is added to precipitate iron salts. The liquor is concentrated in open copper vessels or in boiler steel kettles (162 B.P) and gradually cooled to 120°C, when remaining kieserite separates out in the same vessel or in separate settling kettles. The clean hot liquor is filled into drum when fused magnesium chloride ($MgCl_26H_2O$) solidifies to a hard mass. The quantity of magnesium chloride produced is considered satisfactory both by consumers in and abroad.

Sulphate ions present as magnesium sulphate interfere in winning of pure potassium chloride by solar evaporation of bitterns. The known processes for the removal of sulphate ion are (1) addition of lime (2) addition of calcium chloride (3) partial removal by refrigeration.

The first method is based on the chemical reaction between $MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$. Slaked lime is added to 32° Be bittern equivalent to sulphate radicle and magnesium sulphate is converted to magnesium hydroxide and is removed along with co-precipitation of $CaSO_4$. The liquor contains mainly KCl, $MgCl_2$ and NaCl. This is concentrated by heating to obtain carnallite. The difficulty of this process is the tedious nature of the separation and recovery of $Mg(OH)_2$ and $CaSO_4$ from co-precipitation.

In the second method, calcium chloride is used to precipitate out as calcium sulphate leaving behind in the liquor $MgCl_2$, KCl and NaCl. Carnallite is obtained either by solar evaporation for artificial heating. Due to increase in concentration of magnesium chloride, carnallite separates out at lower density of 34° Be bittern. The only drawback in this process is the use of a costlier chemical viz. calcium chloride in order to obtain less costly chemicals which offsets the utility of the process for economical reasons unless calcium chloride is available as by-product in the a nearby soda-ash plant. Dr. Kane[12,13] and his co-workers have described the process in full and by the use of distiller waste liquor, the authors are advocating that the process will be suitable and economical since carnallite can be obtained by solar evaporation alone and the cost of the fuel is saved for artificial heating. In another process[14] commercial grade calcium chloride (95% $CaCl_2 \cdot 2H_2O$) is used for desulphation of bittern and carnallite was obtained by forced evaporation.

The California Chemical Corp. follows a similar process in which the sulphate of magnesium is precipitated out as calcium sulphate by reacting calcium chloride with raw bittern. Carnallite is crystallised at 35°Be from which both magnesium chloride and potassium chloride are recovered in the conventional method. The required calcium chloride for the process is obtained by treating a part of sulphate free bittern with calcium hydroxide. From the precipitate of $Mg(OH)_2$, light magnesia (MgO) or periclase is obtained by calcination in rotary kilns. In all these processes the concentration of potassium chloride in the filtrate is very low. This results in large volume of the solution which is required to be evaporated even though calcium chloride is used in a concentrated form. To avoid encounter most of the difficulties in earlier work, desulphation was effected in this Institute by employing saturated mixed salt solution as well as mixed salt in solid form[15].

Carnallite is directly obtained from Dead Sea bittern by solar evaporation. Dead sea brine is rich in magnesium chloride and is available at high density. It contains less amount of sulphate (half) so that the carnallite is not contaminated with magnesium sulphate. No precipitant is used as the sulphate content is very much less and does not separate out with carnallite at 34° Be.

Similar conditions exist~~s~~ at Udoo, Kharaghoda. Udoo bittern after the removal of sodium chloride contains a small amount of sulphate and further concentration to 34°Be by solar evaporation, carnallite separates out. The Udoo bittern also contains a high percentage of magnesium chloride with the result, that carnallite can be separated out at lower density similar to Dead Sea. Further evaporation yields high purity magnesium chloride ($MgCl_2.6H_2O$) a valuable by-product for the magnesium metal industry.

In the conventional processes one can observe that the fuel cost is considerable. If all the products are not recovered the processes are not economical. Therefore, an economical process has been worked out at this Institute whereby mixed salt is obtained by natural solar evaporation. Mixed salt containing KCl, NaCl, $MgSO_4$ and $MgCl_2$ is extracted at 110°C by employing 36° Be bittern, the end liquor obtained in salt works. Earlier, there has been no suitable method to obtain potassium chloride in presence of sulphate ion. Residue contains magnesium sulphate and sodium chloride which does not go into solution. On cooling the clear hot liquor, carnallite separates out. The carnallite is treated in the conventional way to obtain potassium chloride. In this process, minimum amount of fuel is used just to raise the temperature to 110°C (sensible heat) and no chemicals are used to desulphate the bittern. In order to improve the economics of the process, magnesium sulphate and sodium sulphate are recovered as by-products by chilling process. The process forms the matter for this thesis and is reported in Section II. This new process on a commercial scale has been put up at Kandla to determine the economics of the process.

Other potash salts also can be manufactured directly from mixed salt. Potassium sulphate is preferred to potassium chloride for use as a fertiliser for certain crops. Simple processes have been worked out in this Institute.

In one of the process syngenite, a double salt of K_2SO_4, $CaSO_4$ containing 50 per cent K_2SO_4 has been prepared by mixing gypsum with mixed salt and by leaching with water to remove sodium chloride and magnesium chloride.

In the second process potassium sulphate has been prepared from mixed salt by three stages through the formation of schoenite. In the first stage kainite ($KClMgSO_4$ $3H_2O$) is obtained by floation of mixed salt thereby eliminating sodium chloride and magnesium chloride; 2) in the second stage, the floated mixture is treated with water at room temperature to obtain potash schoenite ($K_2SO_4MgSO_4$ $6H_2O$); 3) in the third stage the potassium schoenite is treated with excess of potassium chloride to obtain potassium sulphate.

In the other process mixed schoenite consisting of ammonium and potassium schoenites free from chloride have been prepared by treating mixed salt with ammonium sulphate. Nitro-magnesia as fertiliser has been prepared by treating the sel's mixts with ammonium sulphate. The dehydrated mixed schoenite product contains N 5.0 per cent K_2O 15.0 per cent MgO 4.4 per cent; while the nitro magnesia product contains 6.7 per cent N, 10.5 per cent MgO and 1.5 per cent K_2O. These fertilisers, because of their soluble magnesia contents have certain advantages over the conventional nitrogen and potassium fertilisers.

By treating the mixed salt with aluminium sulphate solution, the entire potash content of mixed salt is recovered in the form of a valuable chemical as potash alum K_2SO_4 $Al_2(SO_4)_3 24H_2O$. Potassium sulphate is formed in situ by the reaction between potassium chloride and magnesium sulphate present in the mixed salt; potassium sulphate can be obtained by chemical treatment or by calcination. The process forms a part of this thesis and is reported in Section II.

Since the term potash is applied to many potash salts used in industry and agriculture it is customary to compare such products on the basis of equivalent K_2O content and they are sold on the basis of the units K_2O content. The unit is defined as one per cent per ton or weight of 20 pounds. Thus pure potassium chloride is considered to be 63 per cent equivalent K_2O (K_2O/ 1 KCl) and potassium sulphate is considered to be 54 per cent K_2O.

As seen above only 40,000 tonnes of potassium chloride or its equivalent potassium sulphate can be manufactured annually from bitterns, on the basis of practical recovery on the present production of common salt in the country. The requirement of potash fertilisers alone is approximately 2 lakh tonnes ~~(see Table 10)~~. Thus availability of potassium chemicals from bittern or mixed salt as a source is limited. Sea water is an unexhaustible source of potassium chemicals, which are recovered by employing a selective reagent.[72] Potassium salt of hexanitrodiphenylamine is sparingly soluble while sodium, magnesium or calcium salts are soluble. The methods employing an agent selective for potassium normally requires regeneration and reuse of the agent in a recycling process; however, in the regeneration step there is a considerable choice, to produce potassium salt as desired. In many cases the regeneration is carried out with an acid, thus selective agent process offers the useful possibility of recovery of potassium as the nitrate salt, particularly suitable for fertiliser. Probably the most feasible method tested for potassium recovery involves the use of a highly selective chelating or sequestering agent. The first of these reported is dipicrylamine[15] which forms stable complexes with metal ions in aqueous solutions but is selective since only the potassium complex is insoluble.

This method has been studied extensively by Norsk Hydro of Norway and the results are described in patents.[16,17] As reported recently, however Norsk Hydro built[18,19] a pilot plant for this process in Norway in about 1942 and another in Holland after World War II. In a later detailed study, Massazza[19] and Riva using batch tests with solar evaporation bitterns have reported potassium recovery as high as 99 per cent with dipicrylamine method. This chelation method is at present under study at Yale University[20].

A cryѕtalliser for this chelation process has been patented[21] and other nitrated diphenylamines[22,23] have been found to be effective. An ion exchange[24] process to produce HCl for use in regenerating the chelate has been suggested; raw sea water is passed over cation resin in the hydrogen form to absorb potassium and other metals and to produce HCl. Regeneration of the resin is done with nitric acid to yield a solution containing potassium nitrate. This ion exchange method does not appear economically feasible, as nitric acid is used to produce hydrochloric acid and as the potassium solution requires considerable purification. A more interesting use of ion exchange is studied in laboratory test by passing sea water over an exchange material formed by placing dipicrylamine on active carbon.[25]

Potassium has also been precipitated from sea water using sodium bismuth thiosulphate[26]. Recovery and regeneration is carried out by acidifying the potassium precipitate, separating the bismuth and converting the bismuth to thiosulphate form. Potassium chlorate[27] has been precipitated from bitterns by addition of calcium chlorate. After subsequent removal of magnesium with calcium hydroxide the filtrate is reoxidised electrically to regenerate calcium chlorate. One Japanese patent suggests a electrodialysis[28] process for potassium recovery. The work on precipitation of potassium from sea water using selective agent dipicrylamine forms part of this thesis, and is reported in Section II, chapter 5.

Recovery of mixed salt from bitterns and extraction of carnallite from mixed salt with 36° Be bittern and by-product recovery are based on van't Hoffs solubility relationship of oceanic salt system: $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4-H_2O$ at 25 & 83°C. Decomposition of carnallite is based on $KCl-MgCl_2-H_2O$ system at 25°C; recrystallisation of impure potassium chloride is based on $NaCl-KCl-H_2O$ at 30 and 110°C; recovery of epsom salt from sel's mixts is based on mutual solubilities of $MgSO_4$ - NaCl and $MgCl_2$; while recovery of sodium sulphate from sel's mixts solution is based on reciprocal salt pair system $2NaCl + MgSO_4 = MgCl_2 + Na_2SO_4$. Low solubility of potassium alum and the utilisation of sulphate from magnesium sulphate to convert potassium chloride to sulphate, is utilised to develop another process for recovering another potassium chemical from bitterns. All these are subject matter of the present thesis and are reported in Section II.