

MARINE BASED ELECTROCHEMICALS AND METALS

K.C. NARASIMHAM and P.S. DESIKAN

Central Electrochemical Research Institute, Karaikudi-623 006

The oceans of earth are an aqueous, electrolytic solution, covering about 72% of the earth's surface. The dissolved materials in sea water may be broadly classified into (i) major constituents (ii) trace elements (iii) nutrients and (iv) organic materials. The five major constituents viz. Cl^- , Na^+ , SO_4^{2-} , Ca^{++} and Mg^{++} account for more than 98% by weight of its dissolved salts in sea water.

This paper describes the utilisation of some of the above constituents to produce chemicals and metals by electrolysis. Details on the production of alkali-chlorine, halates, perhalates, magnesium metal, sodium metal and lithium for which the chemicals from sea water are utilised as raw materials, are described.

Key words: Marine electrochemicals, chlor-alkali, halates, perhalates, sodium, magnesium, lithium

INTRODUCTION

The oceans of earth are an aqueous, electrolytic solution, covering about 72% of the earth's surface. It is reported that there are 300 million cubic miles of sea, weighing roughly 4000 million tons and containing on the average 166 million tons of dissolved salts or ions as shown in Table I.

Lithium content in the sea is of the order of 0.2 ppm. Aluminium is present in sea water to the extent of 0.6 to 2.4 ppm.

TABLE-I: Dissolved salts of sea

Salts	Tons	Elements	Tons
NaCl	1,28,284,400	F_2	1,400
MgCl_2	17,946,500	Ba	900
MgSO_4	7,816,000	I_2	100 to 12,000
CaSO_4	5,939,700	As	40 to 400
K_2SO_4	4,068,200	Rb	200
CaCO_3	579,800	Ag	~ 50
MgBr_2	358,300	Au	25
		Ra	5 grams

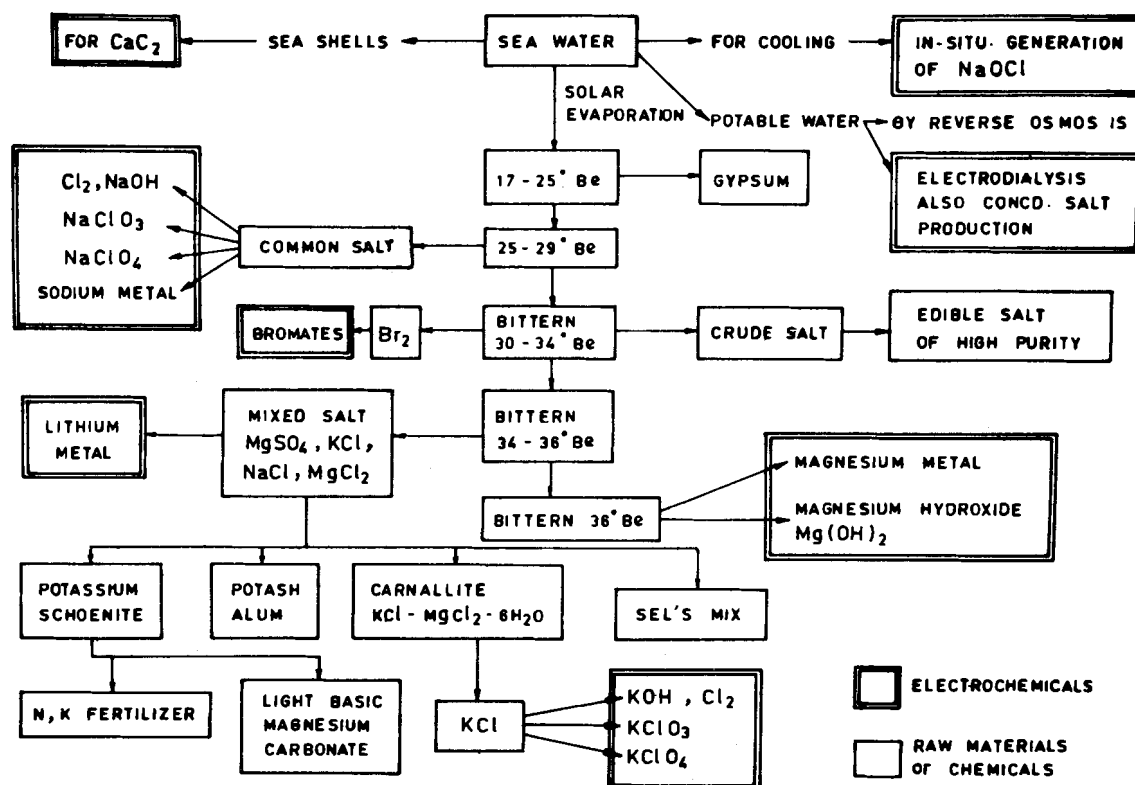


Fig.1

The dissolved materials in sea water may be broadly classified into (i) major constituents (ii) trace elements (iii) nutrients and (iv) organic materials. The five major constituents viz Cl^- , Na^+ , SO_4^{2-} , Ca^{++} and Mg^{++} account for more than 98% by weight of its dissolved salts in sea water and Table II gives these constituents in parts per 1000 parts of sea water.

TABLE II : Major constituents of sea water

Constituents	Parts per 1000 parts of sea water
NaCl	27.2
MgCl_2	3.8
MgSO_4	1.7
CaSO_4	1.25
K_2SO_4	0.85
CaCO_3	0.12
MgBr_2	0.08
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Thus the sea water can be used for the production of various industrial chemicals as well as raw materials for other industries, as indicated in Fig. 1.

In this paper, the utilisation of some of the above chemicals as raw materials in the electrolytic production of chemicals and metals will be highlighted by describing the technologies involved in the production of such chemicals like alkali-chlorine, halates, perhalates and metals like magnesium, sodium, lithium etc.

MARINE BASED ELECTROCHEMICALS

Sodium chloride which is obtained in large quantities at 25-29° Be becomes the potential raw material for a number of electrochemicals. Other electrochemicals make use of potassium chloride and magnesium salts. The shells that are available contain very pure calcium carbonate and partly become the source for the production of calcium carbide by thermal method.

Although sea water cannot be directly used for most of the purposes, yet the possibility of converting the sea water into potable water by desalination techniques which also include electrodialysis, cannot be ruled out. When sea water is used for cooling purposes, the in situ electrolytic production of hypochlorite to avoid fungal marine growth on heat transfer surfaces is resorted.

Electrochemicals based on sodium chloride

Caustic soda - chlorine: The manufacture of caustic soda and chlorine in India which was established on a firm footing, is taking rapid strides. India's production of this chemical is around 0.8 million tonnes as against 12 to 13 million tonnes in U.S.A.

Two distinct process technologies viz mercury cell process and diaphragm cell process have been in operation for the production of caustic soda. This industry needs not only high capital resources but also large quantity of electrical energy. While the consumption

of electrical energy for electrolysis alone is about 3000 kWh/tonne of caustic soda, the range of investment stands between 200 and 300 million rupees for a plant of 100 to 200 tonnes of caustic soda per day. The twin objectives of this industry today are energy conservation and pollution control. One of the developments towards the energy saving to this industry was the emergence, in the early sixties, of the titanium based metal anodes, which replaced the more easily disintegrated graphite anode.

This technological break-through coupled with the recognition of the evil effects of mercury pollution on the environment accelerated further developmental efforts resulting in the advent of ion exchange membranes of perfluoro-type, as diaphragm material. This new technology viz. membrane cell technology is ideally suited for further developments both from the view points of energy saving and avoiding the mercury emission.

In order to utilise the special properties of the membranes for the electrolysis of alkali chlorides to produce caustic soda or caustic potash, various designs of cells have been evolved. The different designs use also different optimum working conditions. For large scale production, two types of designs are possible: (a) bipolar and (b) monopolar designs. The bipolar type of cell arrangement is preferred where relatively small production is envisaged. On the other hand, for large capacity plants, a monopolar arrangement is preferable. The advantages and disadvantages of this recently developed membrane cells versus the conventional mercury and diaphragm cells for the production of chlor alkali are indicated in Table III.

The main factors which will determine the long performance of the membrane depend on membrane handling and contact with metal, cell design, brine hardness, brine sulphates, corrosion, electrolyte concentration and temperature. Further improvement of membrane technology led to the development of solid polymer electrolyte (SPE) electrolysis technology for the production of alkali-chlorine jointly by General Electric (USA) and De Nora (Italy). In this, the perfluoro cation exchange membrane (0.25 to 0.3 mm) acts as a solid electrolyte. The energy consumption of different cells in chlor-alkali industry is given in Table IV.

The membrane cell and SPE electrolyser require very high purity salt with Ca^{++} and Mg^{++} contents to less than 50 ppb, which warrants a secondary brine purification step. For this, special ion exchange resin of chelate type is employed to reduce the multivalent ions as the second stage of purification of brine.

Further improvements have recently been made in the composition of metal anode with a view to increase the coating life in the production of chlor-alkali. Catalytic hydrogen cathode and oxygen consuming cathode are some of the further improvements being tried to reduce the energy consumption in the chlor-alkali industry.

Sodium chlorate and sodium perchlorate

About 4,30,000 tonnes of sodium chlorate are produced each by U.S.A. and Canada and about 85% of the same is utilised for bleaching of paper. The market for sodium chlorate has not well developed in India, though there is a good potential. Only about

TABLE-III: Membrane cells vs mercury cells and diaphragm cells for the production of chlor-alkali

Membrane cell vs Mercury cell	Membrane cell vs Diaphragm cell
Advantages	
(i) Eliminates mercury handling	(i) Eliminates asbestos handling
(ii) Nil hydrogen in chlorine	(ii) Nil hydrogen in chlorine
(iii) More adaptable to small installations	(iii) Nil chlorates and sulphates in caustic
(iv) Smaller brine area system	(iv) Low chloride grade caustic
	(v) Small evaporation required for 50% caustic
	(vi) No need for salt separation equipment
	(vii) Lower energy consumption.
Disadvantages	
(i) Very pure brine required	(i) Requires solid salt
(ii) Some evaporation required to produce 50% caustic	(ii) Very pure brine required

TABLE - IV: Energy consumption for different chlor-alkali cells

	Mercury	Diaphragm +	Membrane	AZEC*	SPE
Current density (KA-m ⁻²)	12	2	3	4	3
Current efficiency (%)	96	95	95	94-95	94-95
Cell voltage (V)	4.3	3.4	3.35	3.02	2.75
AC power for					
Electrolysis++(kWh/t.NaOH)	3060	2420	2410	2140	1950
Auxiliaries (kWh/t.NaOH)	80	210	95	95	95
Steam*** (kWh/t.NaOH)	25	650	250	180	225
Total (kWh/t.NaOH)	3165	3280	2755	2415	2270

+ : Modified asbestos and expandable anodes

++ : At 98% AC/DC conversion efficiency

*** : To raise concn. of NaOH to 48% (250 KWH(AC)/tonne steam)

* : Calculated from the published data

4000 to 5000 tonnes of sodium chlorate per annum are produced in India. The raw material is purified sodium chloride and is electrolysed in a diaphragmless cell with titanium based metal anode and mild steel cathode. Some of the recent developments in the technology of the process for making sodium chlorate are: (a) use of modular construction of electrolyzers of monopolar or bipolar configurations with the assembly of the electrodes vertically or horizontally - a compact system with minimal electrical connections and with a high chlorate output results (b) hydrogen gas produced in the cell is utilized for the rapid circulation of the electrolyte and (c) provision of an external reactor for individual cells or groups of cells, where the secondary chemical reactions are allowed to take place culminating in the formation of chlorate and where hydrogen gas is separated. With these developments D.C. energy consumption has been brought down to 4800 to 5500 kWh

per tonne of sodium chlorate with anode current density ranging from 1.5 to 3 KA. m⁻². Sodium chlorate, being highly soluble naturally becomes the raw material for making other chlorates and perchlorates also. The operating conditions of the cell are given in Table V.

In view of its high solubility, sodium perchlorate is the starting material for making other strategic perchlorates like potassium and ammonium perchlorates needed for Defence and as solid fuel for rockets and this in turn is produced either from sodium chlorate or directly from sodium chloride. When platinum is employed as anode, the preparation of sodium perchlorate is invariably from sodium chlorate. However, the successful development of lead dioxide anodes not only provides a cheap substitute for costly platinum but also enables the preparation of perchlorates either from sodium

TABLE-V - Operating conditions for halates

Conditions	Chlorates		Bromate	Iodate
	Sodium chlorate	Potassium chlorate		
Electrolyte:				
Inlet	Satd. NaCl	KCl 270 g/l KClO ₃ -30g/l	Satd. NaBr (Or) K Br	I ₂ in NaOH or KOH
Outlet		KCl 270 g/l KClO ₃ -80g/l		
Addition agent	Chromate (2g/l)		Chromate (2g/l)	---
Anode	Graphite, magnetite lead dioxide or metal anode		Graphite, lead dioxide	Graphite, lead dioxide
Cathode	Mild steel		Stainless steel	Stainless steel
Anode C.D. (A.dm ⁻²)	2-5 with graphite & magnetite 5-10 with lead dioxide 20 with metal anode		2-5 with graphite 15-20 with lead dioxide	2-5 with graphite 15-20 with lead dioxide
Temperature (°C)	50-70		55-60	40-50
pH	6-7		8	8
Current efficiency (%)	75-90		90-95	75-80
Energy consumption kWh(DC)/kg	4.8 - 6.5 (Depending on the anode)		4.0-4.5	3.0-3.4

TABLE-VI: Operating conditions for perchlorate cell with platinum and lead dioxide anodes

Conditions	With Pt anode	With PbO ₂ anode
Cathode	Mild steel	Stainless steel
Electrolyte	Satd. NaClO ₃	Satd NaClO ₃ or Satd. NaCl
Addition agent	Chromate (2g/l)	NaF (2g/l)
Anode C.D. (A.dm ⁻²)	30-40	15-20
Temperature (°C)	55-60	50-55
pH	6-7	6-7
Current efficiency (%)	75-80	70-75% for NaClO ₃ to NaClO ₄ and 55-60% for NaCl to NaClO ₄
Energy consumption (Kwh (DC)/kg)	3.0-3.5	3.0-3.5 for NaClO ₃ to NaClO ₄ and 7.5 - 9 for NaCl to NaClO ₄

chlorate or from sodium chloride; in the latter case the novelty being the production of perchlorate in the same cell without alteration of operating conditions or recourse to intermediate processing at the chlorate stage. The operating conditions are given in Table VI.

Electrochemicals based on potassium chloride

Potassium hydroxide (Caustic potash)

The same cells used for the production of sodium hydroxide or caustic soda and chlorine are employed for the production of caustic potash employing pure potassium chloride as the raw material. However, the type of cation exchange membrane differs from the one that is employed in the membrane cells for the production of caustic soda.

Potassium chlorate and potassium perchlorate

Potassium chlorate has gained much importance in the Indian electrochemical industry because of its continued demand in the manufacture of safety matches. Although the same electrolytic cells employed for sodium chlorate production are used for the production of potassium chlorate, the composition of the electrolyte is therefore determined from the solubility of potassium chlorate in potassium chloride solution, as the potassium chlorate is less soluble in water itself. Interelectrode spacing will be between 6 and 9 mm for potassium chlorate cells unlike 1 to 2 mm gap for cells producing sodium chlorate, thereby giving allowance even during the rapid crystallisation of potassium chlorate in the cell arising out of any lapse in maintaining temperature and composition of electrolyte or due to power failure. The operating conditions are given in Table V.

Potassium perchlorate, being poorly soluble, is easily prepared by the double decomposition of electrolytically prepared sodium perchlorate solution with the stoichiometric quantity of potassium chloride solution.

Electrochemicals based on bromine and iodine

Bromine can be produced from sea water and the same can be converted into bromide. The bromides of sodium and potassium become the raw materials for the production of corresponding bromates electrolytically. Bromates are needed for bakeries to improve the baking characteristics of the bread and also in the hair-wave preparation. The electrolytic cell is diaphragmless and consists of graphite or lead dioxide anode and stainless cathode. The operating conditions are shown in Table V.

With the introduction of new regulations of iodising the common salt to avoid goitre trouble for people, the demand for potassium iodate has increased. This salt is produced electrolytically from the electrolyte consisting of iodine obtained from sea weeds and mixing it with potassium hydroxide solution. An anode of either graphite or lead dioxide or platinum anode, stainless steel cathode without diaphragm are employed. The operating data for the production of potassium iodate are also given in Table V. On further oxidation of potassium iodate at lead dioxide anode, potassium periodate is obtained which is used as an oxidant in the production of dialdehyde starch from starch.

Electrochemicals based on magnesium chloride or bitterns

Magnesium hydroxide of pharmaceutical grade has been prepared electrolytically in an easily filterable form by using sea bitterns or any other source for magnesium chloride as raw material.

Other possible electrochemical reactions

The sea shells can be a good source of calcium carbonate and partly become the raw material in the electrothermal production of calcium carbide.

Due to large quantities of dissolved salts in sea water, it cannot be directly used as potable water. But in case of necessity, the sea water can be converted into potable water through reverse osmosis and electrodialysis techniques. While the former does not use electricity, the latter is an electrolytic technique and has limitations, namely, that the technique may not be economical when the salt content exceeds 6000 ppm. As demineralization proceeds, the electrical resistance of diluate increases progressively, so that 400 to 600 ppm is the normal economic lower limit. The electrodialysis is a membrane process in which the electric current is utilised to effect the removal of the salt ions. An arrangement of alternating anion and cation permeable membranes between two end electrodes enables an electrolyte system to be split into two, a concentrate and a diluate by the movement of ions when a potential is applied. Though this technique is used in India for getting potable water, the same technique is used in Japan to produce brines that have almost the same concentration as the brines produced by solar evaporation. A suitable membrane called Univalent selective ion exchange membrane has been developed through which only univalent ions are transferred to produce concentrated solution by suitably adjusting the operating conditions. In Japan, electrodialytic concentration of sea water is preferred on an industrial scale to produce sodium chloride brines which are further concentrated by evaporation to produce table salt. The quantity of sea water needed for the production of salt in this process is 100-200 m³ (264,000 - 528,000 gal) per ton of salt. The sea water must be free from turbidity, microorganism, organic matter etc.

When sea water is used for cooling purposes, fungal marine growth occurs on heat transfer surfaces. The generator to produce in situ hypochlorite to destroy such a fouling growth is included in the lime. The cell can be bipolar or monopolar, with lead dioxide anodes or preferably metal anodes to give compactness consistent with good efficiency.

MARINE BASED METALS

While a large number of metals are found in sea water including those like uranium and gold, it is confined to those metals which are practically feasible to recover by electrochemical techniques.

Sodium

Sodium metal is naturally most abundant metallic element found in sea water. The requirement of sodium metal for human utilisation is very small. The metal is required as a chemical intermediate for the preparation of certain compounds like vitamins or tetra ethyl lead, as a reductant for recovery of certain metals like titanium

and uranium and as a coolant in nuclear reactor. The technology for the production of sodium is a well established one which consists in the fused chloride electrolysis. The sea salt when it is used for this purpose should be desulphated and completely dried. The Down's cell is a well known design for the electrolyser and consists of graphite anode and steel cathode with steel gauze as diaphragm. Sodium comes to the riser pipe and collected in mineral oil and also stored in oil. The technology for sodium metal has been perfected by CECRI and is being utilised on an industrial scale in the country, using 10000 A capacity cells.

Magnesium

The use of seawater for production of magnesium metal has been practised for over 60 years by Dow Chemicals of USA. The magnesium content of sea water is about 0.1% and hence Dow's facility pumps millions of gallons of sea water for its plant to recover the magnesium first as its hydroxide by precipitation with lime. Thus for 1 tonne of magnesium to be recovered about 1000 m³ of seawater has to be handled. From this point of view the tropical countries like India are better placed because in the salt farms along its coast, the magnesium content in the seawater could be concentrated upto 10% from 0.1% i.e. a hundred fold increase with the use of direct solar energy with practically no cost involved. This advantage could however be taken in certain limited number of salt farms where the weather conditions favour the concentration of bitterns from 29° Be to 36° Be. At 29° Be the common salt separates. Concentration of the bittern upto 36° Be is necessary to remove other residuary materials like KCl and part of the sulphates which get crystallised out at various stages of concentrations. It has been observed that only in areas where there are minimum rainfall, least humidity and maximum wind velocities, this concentration upto 36° Be is possible. Areas like Tuticorin and Gujarat where most of the Indian sea-salt is produced

has been found suitable for this purpose.

The identification of 36° Be bitterns as a suitable raw material for magnesium recovery and the development of most updated electrolytic cell for electrolysing MgCl₂ by CECRI has placed India in a more advantageous position for production of magnesium. Thus it could be seen that the total energy requirement for 1 tonne of magnesium from raw material to end product by CECRI's know-how works out to be 259 x 10⁶ Kcal as against 358 x 10⁶ Kcal by Dow's process. A commercial plant based on CECRI's technology is being set up at Valinokkam.

Lithium

Lithium metal is growing in importance in view of its recently found new uses as in Al-Li alloys, lithium batteries etc. The terrestrial resources for this metal are meagre. In spite of the very very small amount of lithium in sea, it will be worthwhile to explore the means of recovering it from the marine sources. Even though in the sea water itself lithium is of the order of 0.2 ppm, certain brines in the inland wells near sea could contain as high as 200 to 400 ppm of lithium. According to U.S. based literature, the inland brines are classified into three types, evaporites, geothermal and oil field brines. The brine process is reported to be the extraction method of choice for the purpose due to large resources and energy advantage. Though the lithium content is as low as 200 ppm still its extraction appears to be economically viable. The presence of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Ba⁺⁺⁺, Cl⁻, SO₄⁻² restrict the loss of recovery. Since lithium is more soluble, by concentration other ions are removed.

Fig.2 gives the flow sheet describing the method adopted for extraction of lithium from brine.

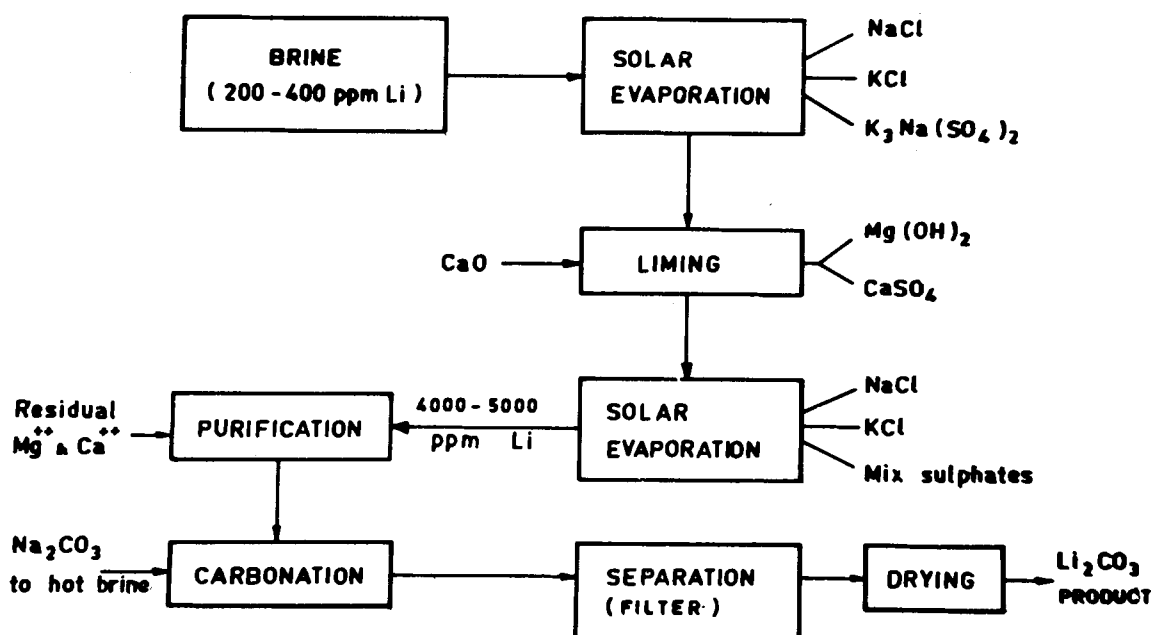


Fig.2a: Flow diagram for lithium production from brine (containing low concentration of lithium)

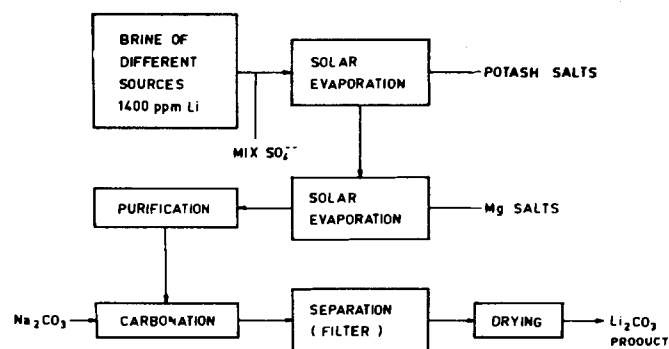


Fig.2b Flow diagram for lithium production from brine of different sources (containing high concentration of lithium)

Fig:2b

Geothermal brines

These brines containing 150-400 ppm lithium have high Ca^{++} content. Separation of lithium from Ca^{++} is difficult and research work is being carried out. Apart from Ca^{++} the requirement of reinjection of fluid into aquifer also exists. Reinjection eliminates processing using solar evaporation. Chemical means have to be employed to extract lithium.

Bureau of Mines have developed a process wherein the brine is used to generate electricity and the post flash brine is available for mineral extraction and reinjection. The post flash brine is treated with lime to remove heavy metals followed by treatment with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Lithium is separated as LiAlCl_4 complex. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is recovered by sparging LiAlCl_4 with HCl . Li^+ is recovered in the brine. Lithium containing brine is spray dried. Solids containing Li and Ca are leached with THF (tetra hydro-furane) to remove Ca^{++} . LiCl is purified using oxalic acid to remove excess Ca^{++} . It is estimated that the cost to recover LiCl is almost equal to the current selling price. Disadvantages of this process are multiplicity of processing steps and cost of expensive raw materials.

Many oil field waters contain Li (50 ppm). These brines are processed to get Br_2 , Mg.

Dow has described a process to selectively extract LiCl by ion exchange using anion exchange resin composites with AlCl_3 or $\text{Al}(\text{OH})_3$. Lithium containing brine is contacted with resin to form lithium aluminate dispersed in resin. Lithium is washed from resin with dilute lithium solution using a non-competitive ion such as

sodium. Multistep anion-exchanger can be employed to concentrate lithium in solution. Lithium is precipitated as LiCO_3 . This process is not yet commercialised. By this process multiple products are removed from brine.

Lithium carbonate recovered from the various sources is first converted into lithium chloride by treatment with hydrochloric acid and subsequent drying to get anhydrous lithium chloride. A melt of lithium chloride with a mixture of potassium chloride is electrolysed in a modified Down's type cell between graphite anode and steel cathodes to recover molten lithium metal. A 500A cell for production of lithium has been successfully run at CECRI.

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