Development of Electrochemical Industries Utilising Sea Water as Raw Material *

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ABSTRACT

THE future prospects of various methods proposed or practiced for recovering sodium, potassium, magnesium and calcium compounds from sea water are discussed with special reference to the development of electrochemical industries in India. The recovery of the sulphate content of the bitterns as sulphuric acid or sodium sulphate employing byproduct hydrochloric acid, from organic chlorination reactions indirectly, is bound to be more economical than the other methods of utilising the sulphate content. This procedure enables the economical production of pure bromine, potassium chloride, sodium chloride and magnesium chloride from bitterns. This in turn will encourage the expansion of the aqueous sodium and potassium chloride electrolysis and also fused salt electrolysis of sodium and magnesium chlorides. Thus the development of electrochemical industries can be intimately connected with the economical production of many heavy chemicals.

Sea water is practically an inexhaustible source of sodium, potassium, magnesium and calcium compounds. Sodium chloride recovered from the sea is utilised for edible purposes as well as in industries. The manufacture of caustic soda and chlorine by the electrolysis of brine is one of the important electrochemical industries. Caustic soda is consumed in large quantities in the manufacture of rayon, soap, paper and in many other processes. Soda ash produced by reacting electrolytic caustic with carbon dioxide finds application in the manufacture of glass, detergents, soap, textiles, water softeners etc. Electrolytic caustic can also be advantageously employed in the production of sodium sulphide by reacting with hydrogen sulphide or with sulphur dioxide to produce sodium sulphite, bi-sulphite and through them sodium hydro-sulphite and sodium thiosulphate, to meet the demand for these sodium chemicals in paper, leather, metallurgical, dye, photographic engraving and textile industries. Sodium silicates for use as adhesives, detergents, metal cleaners, fire proofing and sizing can be manufactured from electrolytic caustic. In a country like India sodium phosphates for use in detergency, water softening etc., can be produced economically as byproduct in the production of rare earth metal hydroxides from monazite. The electrolytic caustic can also be directly neutralized with phosphoric acid to produce sodium phosphate. The production of sodium carbonate from electrolytic caustic and its subsequent employment for decomposing gypsum to produce sodium sulphate can meet the demand for sodium sulphate in kraft pulp manufacture, synthetic detergents, dye industries etc.

Not less than 85% of the total chlorine is now obtained by the electrolysis of sodium chloride solutions. The demand for chlorine is so great that not only the conversion of electrolytic caustic to other sodium chemicals as indicated is justified while expanding the production of chlorine by the electrolysis of brine, but also the efficient utilisation of byproduct hydrochloric acid from organic chlorinations has become of utmost importance. Any amount of byproduct hydrogen in the electrolysis of brine can be utilised profitably for hydrogenation purposes and also in the production of synthetic ammonia. Chlorine is employed in the manufacture of pulp and paper; in textile bleaching; water treatment; sewage purification; lead tetraethyl; ethylene glycol; phenol; vinyl and vinylidine polymers; chlorinated rubber and other plastic solvents; insecticides, fungicides, bactericides, herbicides etc. The electrolysis of aqueous solution of sodium and potassium chlorides and the fused salt electrolysis of sodium and magnesium chlorides now practically account for the entire production of chlorine. Hence it is clear that the electrochemical methods of manufacturing heavy chemicals have become important and will replace completely in course of time well established chemical methods for manufacturing them. Although cheap electric power is an essential prerequisite for the expansion of electrochemical industries, the economical recovery of pure chlorides of sodium, potassium and magnesium from sea water is equally important.

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About 3 million tons of solar salt are recovered from the sea annually in India. The production of solar salt is rapidly increasing and production capacity will be increased to 6 million tons within 7-10 years. The bitterns left over in the production of 3 million tons of sodium chloride from sea water by solar evaporation contain 300,000 tons of magnesium sulphate, 480,000 tons of magnesium chloride, and 80,000 tons of potassium chloride. The solar evaporation of bitterns results in the deposition of magnesium sulphate together with sodium chloride and carnallite. A sharp separation with maximum recovery of the various constituents is impossible by a simple procedure. However if the sulphate content of the bitterns is eliminated as calcium sulphate, then the production of pure sodium chloride and carnallite by the evaporation of desulphated bitterns is profitable.

The utilisation of calcium chloride byproduct from different industries offers interesting possibilities for eliminating the sulphate content of bitternas as calcium sulphate. Although calcium chloride can be obtained as a byproduct in the production of potassium chlorate by first preparing the calcium chlorate, yet this chemical method is not to be recommended in view of the fact that it becomes a chlorine consuming industry, whereas the trend is towards the production of more chlorine and not chlorine utilisation. The utilisation of calcium chloride byproduct from ammonia soda process is very profitable not only because the waste byproduct is utilised but also the sodium chloride requirements in the production of sodium carbonate can be minimised through the recovery of sodium chloride normally discharged along with calcium chloride byproduct.[1] (In the production of one ton of sodium carbonate about 0·5 to 1 ton of sodium chloride is thrown out along with one ton of calcium chloride).

A cyclic process involving initially the elimination of sulphate content of bitterns as calcium sulphate can also be considered. A portion of magnesium chloride obtained in the later stage of the process is reacted with calcium sulphide formed in the cyclic process, to precipitate out magnesium hydroxide with the liberation of hydrogen sulphide and simultaneous production of calcium chloride in solution.[2] This calcium chloride solution is employed to desulphate the bitterns and the resulting calcium sulphate is reduced to calcium sulphide for use in the process. The hydrogen sulphide gas can be used as such or converted into sulphur dioxide or sulphur by well known methods. However in a country like India this method of obtaining sulphur cannot compete economically with the production of sulphur as byproduct in the hydrometallurgical cum electrolytic processes for winning of metals from sulphide minerals, such as iron pyrities, copper pyrities, zinc sulphide concentrates, lead sulphide concentrates etc.

The other cyclic processes involving the precipitation of sulphate content of the bitterns as gypsum are the following. A portion of the magnesium chloride obtained in the later stage of the process is treated with calcium oxide or with calcined dolomite[1] to precipitate out magnesium hydroxide. The calcium chloride byproduct of this step is employed for desulphating the bitterns. Although Oyster Shells, Coral lime stones etc., are available for this purpose, yet the advantage in employing calcined dolomite is due to the fact that magnesium hydroxide is recovered both from the sea as well as from dolomite simultaneously. Therefore in places where dolomite is available this procedure will be more advantageous than the sraight precipitation with lime.

From the above it is clear that only three processes for the elimination of the sulphate content of bitterns appear profitable. They are in the following order: (1) The utilisation of byproduct calcium chloride from ammonia soda process, (2) The use of calcined dolomite directly, and (3) The use of calcium oxide.

In order to introduce over all economies in the production of chlorides of sodium, potassium and magnesium from the sea, it is also necessary to utilise the sulphate content of the bitterns profitably. Although precipitated gypsum can be used for all the purposes for which mineral gypsum can be utilised yet is advantageous to use it as pigment in any paint compositions, in printing ink etc. The only other method of advantageously utlising this precipitated gypsum will be to react with magnesium hydroxide recovered from the sea or from calcined dolomite or magnesite and produce magnesium sulphate in solutions with the simultaneous precipitation of calcium carbonate. Not only the demand for magnesium sulphate can be met by this procedure, but also magnesium sulphate can be double decomposed with sodium chloride to crystallize out sodium sulphate at low temperatures leaving behind magnesium chloride solution. For the common requirements of gypsum in cement industry, 70-75% mineral gypsum or purified gypsum recovered from the sea by solar evaporation can be utilised. Similar remarks apply to the use of gypsum in agriculture especially with green manure to produce practically the same effects as ammonium sulphate for important crops like paddy, sugar cane etc.

It has already been pointed out that sulphur can be recovered as byproduct from sulphide

minerals. Hydrogen sulphide is produced as a byproduct in gas manufacture as well as in the cracking of petroleum hydrocarbons. In addition, the demand for sulphuric acid in future will be very limited owing to the fact that concentrated chemical fertilizers are nowadays produced by employing nitric acid for decomposing rock phosphate instead of sulphuric acid. Concentrated chemical fertilizers will be produced by the following procedures. Finely ground rock phosphate is reacted with nitric acid. The resulting calcium nitrate-phosphoric acid is filtered off and treated with potassium nitrate to precipitate out the entire fluorine as potassium fluosilicate. The filtrate from this operation is reacted with ammonium sulphate when calcium sulphate is precipitated. The calcium sulphate is converted back to ammonium sulphate (by reacting with ammonia and carbon dioxide) for use again in the process. Thus a concentrated liquid fertiliser containing a mixture of ammonium nitrate-phosphate can be had economically without the use of sulphuric acid. This mixture in combination with suitable proportions or liquor ammonia and potassium nitrate solution recovered from the sea can meet the demand of fertilisers very profitably. Therefore the use of gypsum in the production of ammonium sulphate in future will also be limited. Thus it is clear that the use of gypsum as a source of sulphur, hydrogen sulphide, sulphur dioxide, sulphuric acid, ammonium sulphate, etc . will be very limited in future and when needed for the purpose, low grade mineral gypsum or purified gypsum recovered from the sea can be utilised. By heating low grade gypsum with coal and clay out of contact with air half the sulphur content of gypsum will be expelled as sulphur and the other half as sulphur dioxide.

Utilisation of sodium chloride

Although we have concluded that economies can be effected in the production of sodium carbonate by ammonia soda process through the utilisation of calcium chloride byproduct with bitterns and the subsequent use of calcium sulphate as described above, yet in view of the fact that the demand for chlorine is very high compared to caustic soda there is justification in reacting electrolytic caustic soda with carbon dioxide to produce sodium carbonate. If sodium sulphate from bitterns can be recovered equally economically by any procedure other than the one suggested earlier, viz., precipitating gypsum and then converting it to sodium sulphate through the intermediate production of magnesium sulphate, then the electrolytic production of sodium hydroxide and its conversion to sodium carbonate can become very popular.

A method for the economical recovery of sodium sulphate from bitterns consists in first precipitating out potassium by adding a highly nitrated amine to bitterns. The precipitate is then separately decomposed with nitric acid to obtain a concentrated solution of potassium nitrate in solution with simultaneous recovery of secondary amine for reuse. After the removal of potassium, the bitterns can be cooled to crystallize out Glauber's salt leaving magnesium chloride solution. This method of recovering potassium is very beneficial because concentrated chemical fertilizer is produced and there is no need to employ potassium chloride or potassium sulphate as fertilizer. However potassium chloride for use in the production of other chemicals can be had by utilising byproduct hydrochloric acid instead of nitric acid to decompose the potassium salt of the secondary amine.

The fixation of the sulphate content of bitterns as sulphuric acid can be accomplished by reacting sodium sulphate recovered from bitterns with byproduct hydrochloric acid gas to obtain sodium chloride with the simultaneous production of sulphuric acid. These procedures for recovering sodium sulphate and or sulphuric acid serve to efficiently utilise the byproduct hydrochloric acid gas from organic chlorination reactions, and thereby encourage the production of more chlorine by electrolysis. Sodium sulphate recovered from bitterns can also be electrolysed to produce caustic soda and sodium hydrogen sulphate. Sodium hydrogen sulphate can then be decomposed with byproduct hydrochloric acid to get sodium chloride and sulphuric acid.

From the above it is very clear that the pattern of chemical industry is bound to change considerably in future. Sulphuric acid will not be employed for the production of fertilizers like superphosphate and ammonium sulphate. It will not be employed also in the production of sodium sulphate and hydrochloric acid, and hence in the production of sodium carbonate, sodium hydroxide, chlorine etc , Bromine will first be recovered from bitterns by passing chlorine through hot bitterns.

Any amount of sodium sulphate, sulphuric acid, potassium chloride or nitrate and magnesium chloride can be recovered from bitterns by the procedures described in this contribution at costs comparable to other methods of producing them from a variety of raw materials. The ammonia soda process for the production of sodium carbonate will be replaced by carbonating the electrolytic caustic soda for the following reasons. (1) The production and utilisation of ammonium

chloride byproduct as such as a fertilizer will not be more economical than the use of mixed fertilisers containing potassium, ammonium nitrate-phosphate, (2) The utilisation of calcium chloride byproduct in conjunction with bitterns will not be more economical than the production of sodium sulphate or sulphuric acid and potassium chloride or potassium nitrate from bitterns, (3) Any amount of magnesium sulphate from sea water can be had from bitterns by first precipitating magnesium hydroxide and calcium sulphate through the use of lime or calcined dolomite as described earlier, and then carbonating suitable proportions of the precipitated gypsum and magnesium hydroxide suspended in water. Magnesium sulphate is obtained in solution and precipitated chalk is a valuable byproduce. If lime or calcined dolomite is not available the precipitated chalk is calcined to supply calcium oxide and carbon dioxide for use again in the process, and (4) Any amount of potassium sulphate can be had by employing sulphuric acid manufactured from bitterns to decompose the potassium salt of the highly nitrated secondary amine.

Even in places where natural gas, coke oven gas, gas from petroleum refineries or coal tar products are not available, the electrolysis of sodium chloride has a bright future, provided electricity is cheap. The anaerobic digestion of waste cellulosic materials can supply methane and carbon dioxide. The carbon dioxide can be employed to convert electrolytic caustic to sodium carbonate. The methane can be chlorinated to get methyl chlorides, chloroform and carbon tetrachloride. The byproduct hydrochloric acid can be employed for the recovery of potassium chloride and sulphuric acid from bitterns as described. The byproduct hydrochloric acid gas can also be employed in the production of vinyl chloride, and chloroprene, the acetylene for this purpose being obtained by rapidly passing methane over a heated contact mass containing alkaline earth salts, oxides of magnesium, beryllium, activated silica etc. By varying the condition ethylene can also be produced and employed for chlorination. Acetylene can also be produced by burning preheated (heated to 400°C) methane and oxygen. In this procedure synthesis gas for use in the production of liquid fuels is obtained as a valuable byproduct.[6] Therefore the future for the electrolysis of sodium chloride is very bright.

The production of cheap salt from sea water as described will also stimulate the expansion in the production of sodium metal by fused salt electrolysis. Thus the demand for sodium in the production of important compounds like lead tetraethyl, sodium cyanide, peroxide, etc., and also in the production of metals like zirconium, titanium etc., (by reacting the anhydrous chlorides of these metals with sodium) can be met. Chlorine will simultaneously be produced economically.

The use of potassium chloride

As already stated the future for the electrolytic production of potassium chlorate and perchlorate with potassium chloride as starting material is very bright compared to the chemical methods of manufacturing them. Potassium chloride for use as fertilizer will be replaced by the concentrated potassium nitrate fertilizer. Therefore it need not be recovered from the sea for this purpose or be converted into potassium sulphate. The electrolytic production of potassium hydroxide and its use in the manufacture of liquid soaps etc., and also its conversion to carbonate, silicate, phosphate and the like will encourage the production of electrolytic chlorine. The use of electrolytic potash in the production of potassium manganate and the subsequent electrolytic conversion of manganate to permanganate will help in the production of chlorine without excess production of caustic. The electrolytic conversion of manganate to permanganate is recommended in preference to the oxidation of manganate by chlorine because the latter becomes a chlorine consuming industry. The use of electrolytically produced potassium hydroxide in the manufacture of potassium dichromate will also serve to produce chlorine without the simultaneous production of caustic

Potassium chloride solutions can be electrolysed employing active carbon electrodes[7] when the potassium salt of hydrogen peroxide is produced at the cathode and chlorine is evolved at the anode. Hydrogen peroxide can be distilled off from the potassium salt of hydrogen peroxide through the use of byproduct hydrochloric acid. This method of producing hydrogen peroxide is recommended not only because it consumes only about $\frac{1}{4}$ or $\frac{1}{3}$ of electric power compared to the widely used anodic process but also serves to utilise byproduct hydrochloric acid and converts it to chlorine. Pure potassium chloride recovered from the sea can be employed to make up the small losses of potassium chloride in the cyclic process.

Utilisation of magnesium chloride

The very pure concentrated solution of magnesium chloride obtained from bitterns as described earlier can be utilised in the production of anhydrous or partly dehydrated magnesium chloride and used in the production of magnesi-

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are bringing out this year book every year, and the 1960 edition is a welcome publication. This handy volume covers the whole field of industrial finishing, and the information is grouped under various headings in tabular form. The first few pages are devoted to workshop practice including safety, handling materials etc. The technology section includes protection, cleaning, polishing, electroplating, metal colouring, wood finishes, paint data and paint application. Under Technical Data official finishing specifications are listed. Buyers' guide and Trade directory, a list of professional institutions and trade associations are included. This volume will be quite useful for all engaged in the field of metal and wood finishing.

—S.K.

Principles of Chemistry, *by* L. A. HILLER, Jr. and R. H. HERBER, published by McGraw-Hill Book Co Inc., New York, Toronto, London, 1960, 435 pages.

"No single text can cover all of the topics pertinent to the field of general chemistry. Selection of topics has been made as a result of experimentation with courses in general chemistry taught at the University of Illinois to students in chemistry, physics, engineering and premedical course and related curricula". This text book, according to the authors, has been written for students taking the kind of course mentioned above.

The book is divided into two major parts - the properties of chemical substances and the dynamics of chemical change. Part I consists of nine chapters: review of fundamental concepts, the covalent bond, ionic bond, the solid state, the kinetic theory of gases, liquids and changes of state, organic chemistry, inorganic compounds and their reactions and the properties of metals. Part 2 is divided into seven chapters: the nature of chemical equilibrium, heterogenous equilibria and the properties of solutions, ionic equilibria in aqueous solutions, chemical thermodynamics, oxidation-reduction reactions, chemical kinetics and catalysis, and radiochemistry and the nuclear properties of matter. A short review of mathematical operations is included as an appendix apart from an index. To stimulate the student's interest in current topics in chemistry a selective bibliography has been added. At the end of each chapter questions and problems have been included to enable the student to check his mastery over the subject.

This text book on chemistry which maintains the quality of printing and format typical of McGraw-Hill publications will be invaluable to the students preparing for pre-professional courses to have a grasp of the principles in inorganic, organic and physical chemistry.

—S. K.

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um metal by fused salt electrolysis. Chlorine is a valuble byproduct.

In conclusion it may be pointed out that the development of electrochemical industries as described in this contribution with sea water as the starting material offers solutions to the problems associated with the economical production of many heavy chemicals.

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