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Chemistry

MAJOR AND TRACE ELEMENT DETERMINATION IN BRINE AND BITTERN

KEY WORDS: Bittern, Brine, Salt, Major elements

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ABSTRACT

As the land based resources are depleting at an alarming rate Seawater is considered as an alternative resource of chemicals. Bittern is the waste material rejected at the solar salt fields after removal of salt from seawater. As the seawater and bittern are rich in valuable marine chemicals these can be utilised for the recovery. Attempts has been made to determine the major and trace elements present in brine and bittern to recover various economically important marine chemicals. Brine constitute more than 98% of dissolved solids. The six major ions constituting 98% of dissolved solid in seawater are sodium ion (Na^+), chloride (Cl^-), sulphate (SO_4^{2-}), magnesium ion (Mg^{2+}), calcium ion (Ca^{2+}), and potassium ion (K^+). A study has been carried out to characterise Seawater Brine and Bittern for possible metal extraction like potassium and magnesium.

Introduction

The Oceans of earth are aqueous, electrolytic solutions, covering about 71 % of the earth's surface[1]. Sea water is a multiphase system consisting of a solution of high ionic strength and suspended particles which include living organisms, their remains, terrestrially derived minerals, and material derived from in situ inorganic processes. The dissolved materials in sea water may be broadly classified into (i) major constituents, (ii) trace elements, (iii) nutrients and (iv) organic materials. It contains an average of 3.5% of various elements in solution and hence each cubic mile of seawater holds 166 million tons of solids. Of the 60 elements reported from seawater nine most abundant elements constitute over 99% of the total dissolved solids out of which sodium and chlorine constitute 85.2% of dissolved solids in seawater[2]. The elements which are in constant proportion to one another are chloride 54.8% of total salt, sodium ion 30.44%, sulfate ion 7.5%, magnesium ion 3.7%, calcium ion 1.2%, potassium ion 1.1%, carbonate ion 0.3%, bromide ion 0.2% and the borate ion 0.07% [3]. As the demand for land based resources are increasing and due to rapid depletion, the emphasis is being shifted to alternate sources that are abundant and unexploited. Seawater that covers 72% of the earth's surface holds about 330 million cubic miles of water and is an important terrestrial renewable resource. The history of extraction processes goes back to the Chinese who started extraction of common salt prior to 2200 BC, after which seawater became the principal source of salt production [4].

With the development of science newer processing techniques for recovery of minerals from seawater have come into play. However, more emphasis has been given to the complete utilization of the seawater and bittern. Seawater bittern is the waste by-product rejected at the common salt manufacturing plants. After the separation of salt between 24-29^{0}Be' density, the left over viscous solution of 29-30^0 Be' is called 'bittern' and the major constituents of which are sodium chloride, magnesium sulfate, magnesium chloride and potassium sulfate along with a small quantity of sodium sulfate, bromide, borax and some other minor constituents[5]. It could be easily imagined the production of huge tonnage (10.8 MT) of bittern from different salt industries of our country are being wasted. Considering it as a cheap source, the strategic metals can be recovered by further evaporation under controlled conditions to get the crude salt and mixed salt. Hence, bittern can be directly processed to recover magnesium, potassium, bromide, boron and other economically important chemicals.

In India, the salt production industries are located at the coastlines of India: the Arabian Sea and the Bay of Bengal. The western coast salt industries are situated in Maharastra and Gujarat, while the eastern coast salt industries are situated in Orissa, West Bengal, Tamilnadu and Andhra Pradesh. Recently the salt and marine chemical industries are passing through a crucial period, arising out of massive shrimp cultivation. For a ton of shrimp produced nearly 1.8 tons of debris is discharged as a result of which the entire seawater gets contaminated and adversely affect the salt farming. If this trend continues one has to think of alternative method of making salt and other chemicals from seawater bittern. With such a rising number of salt manufacturing plants, where the generation of bittern is huge tonnage, the extraction of valuable chemicals or metals will be worthwhile with the help of innovative advance technology. Hence, attempt has been taken in this study to initially make speciation of the available metal values present in brine/bittern before adopting the recovery processes for extraction.

MATERIAL AND METHODS

SAMPLE COLLECTION

The state of Orissa has a long coastline and one would expect large and small salt works dotting the coast producing substantial quantities of salt for industrial and for human consumption. In the beginning of the season the density of seawater is between 1.5^0 Be' (Baume) to 2^{0}Be' and rises to 4^{0}Be' by the end of March. The rise in density which is affected by low wind velocity and high humidity reaches at 25^0/26^0 Be' crystallising the salt. The bottom is left over at the end of manufacturing season (at the end of monsoon season) and collected in deep ponds. The bittern samples were collected from these ponds along with brine in a polypropylene container. The samples under study were collected from Huma, solar salt field, Ganjam, Orissa.

REAGENT

The reagents used for analysis of brine and bittern, viz. EDTA, KOH, NH_4Cl, $BaCl_2$, $AgNO_3$, KSCN, KCl, NaCl, Ferric Ammonium Sulfate, Eriochrome black-T and Pattern Reed indicators are of AnalaR grade. Similarly, HCl, HNO_3, ethyl alcohol, nitro benzene and liquid NH_3used as solventsare of commercial grade.

CHEMICAL ANALYSIS OF BRINE AND BITTERN

Firstly, the brine and bittern 26.5^0 Be' were filtered to remove suspended particles and are used as such without any further pre-concentration. Bittern of 26.5^0 Be' was then subjected to artificial desalination resulting 29^0 Be' which along with the brine was subjected to analysis. The pH and Electrical conductivity were measured. Suitable aliquot of sample were diluted with distilled water and were analysed for the major elements like Mg, Ca, Na, K, SO_4^{2-}, Cl^- and trace elements like Fe, Cr, Ni, Co, Al and Boron.

Measurement of pH and EC

The pH of the seawater and bittern were determined by using pH meter (ORION MODEL 1260) with glass electrode. It was first standardized against freshly prepared buffer solutions of known pH values of required range (pH = 4.0, 7.0, 9.2) and then pH of the sample was measured. The electrical conductance of bittern was measured by ORION MODEL 1260 with Conductivity Bridge using the standard procedure.

Estimation of Ca & Mg

The calcium and magnesium content of seawater and bittern were determined by complexometric titration with EDTA. The diluted sample maintained at pH 10 by adding suitable buffer like NH_4Cl / NH_4OH was titrated against EDTA using Eriochrome black-T indicator for total Ca & Mg. For estimation of calcium 8M KOH is used as buffer for maintaining pH-12 and Pattern Reed Indicator was used. In both the cases colour changes from wine red to blue. The Mg concentration was determined by subtracting the volume obtained for Ca from the total Ca + Mg volume.

Estimation of Sulfate (SO_4^{2-}) (Gravimetric)

The diluted samples were precipitated near its boiling point as barium sulfate ($BaSO_4$) in an acidic medium (HCl) by the addition of barium chloride solution. The resulted precipitate was then boiled, filtered, washed with hot water until free of chloride. Then the precipitate was dried, ignited and weighed as $BaSO_4$.

Estimation of Chloride

Chloride was estimated by Volhard's titration method. The sample solution was treated with an excess of standard silver nitrate and the residual silver nitrate was determined by titration with standard thiocyanate using ferric alum (40% Ferric Ammonium Sulfate with water) indicator. As the AgCl is more soluble than AgSCN, nitrobenzene is added for the coagulation of AgCl. The sample solution was titrated until a permanent faint reddish-brown colouration appears.

Atomic Absorption Spectrometry (AAS)

The elements namely Fe, Mn, Ni, Cr, Co and Sb are analysed by Atomic Absorption Spectrometer (Shimadzu model AA6300) where suitable hollow cathode lamps are used for the absorption of characteristic lines by the analyte and the concentration vs. absorbance plot obeying the Beers - Lamberts law counts the concentrations of the corresponding elements.

Inductively Coupled Plasma Spectrometry (ICP-OES)

The quantitative evaluation of elements like Al, Ti, Si, and B was done by ICP (PERKIN ELMER, PLASMA-400) spectrophotometer. A high temperature (10,000K) Argon Plasma source is used for the excitation of the element and the concentrations are measured as a function of the emission intensity of the emission spectra generated by the particular element.

Estimation of Na & K

The concentration of Na & K was determined by Flame Photometer (ELICO - MODEL CL 22D) using specific filter for the wavelength of particular element. Calibration curves were made with suitable standard solutions made from AR KCl and NaCl and the concentrations of the unknown samples were calculated.

Results and Discussion

Solar evaporation is the cheapest and most economic means for the pre-concentration of sea-bittern. Hence in salt industries sea water is subjected to solar evaporation for recovery of salts. The sea water and the bittern of 26.5^0 Be' collected after salt removal were subjected directly for analysis of pH, EC major and trace element. 1500 ml of 26.5^0 Be' bittern is further subjected to artificial desalination resulting 910 ml bittern of 29^{0}Be' causing an appreciable volume reduction to 60.66 %. This desalinated bittern was also analysed for pH, EC, major and trace elements.

The pH is one of the most important factors, which controls the aquatic environment. All the chemical and biological reactions are directly dependent upon the pH of the system. It is typically limited to a range between 7.5 and 8.4[6]. The pH of collected sea water is 8.15 whereas the 26.5^0 Be'bittern is ~ 6. 949. Similarly, for 29^0 Be' bittern pH is found to be ~ 6.71 as shown in Table 1. Seawater is generally alkaline in nature. This alkalinity is due to the presence of the bicarbonates (HCO_3^-), carbonates (CO_3^{2-}) and the ($H_2BO_3^-$) [7]. During solar evaporation as the bicarbonates and carbonates are removed as $CaCO_3$, the pH of the bittern does not remain alkaline. After removal of salt the 26.5^0 Be' bittern changes to 29^{0}Be' where a slight decrease in pH is observed.

Similarly, the sea water has a very high conductivity due to the amount of total dissolved salts. During artificial desalination or volume reduction the water level decreases with increase of dissolved solids, thus contributing to higher conductivity values[8]. The electrical conductivity of sea water is measured to be 26200 µS/cm whereas it is 515000 µS/cm 26.5^0 Be' bittern due to the volume reduction during solar evaporation. It is dependent upon the ionic concentration[9] and ionic mobility of the mineral content in solution. These conductive ions come from dissolved salts and inorganic materials such as alkalis, sulphides and carbonate compounds[10]. However, the electric conductivity of 29^0 Be' Bittern is found to be 505000 µS/cm showing a lesser value than 26.5^0 Be' bittern. This may be due to the removal of NaCl during artificial desalination from 26.5 to 29^{0}Be'.

Table 1. Comparision of pH and EC of brine and bittern

Parameter	Brine 2^0 Be'	Bittern 26.5^0 Be'	Bittern 29^0 Be'
pH	8.15	6.949	6.71
EC µS/cm	26200	515000	505000

The most abundant dissolved ions in seawater are sodium, chloride, magnesium, sulphate and calcium[11]. The concentrations of these ions are high due to the arrival of more salts by rivers with time. The analysis data for various important elements in brine and bittern are given in Table 2 & 3. It shows that with progressive evaporation of sea brine the concentration of some major elements increases while some decreases. The concentration of major elements like Mg, K and SO_4^{2-} anion increases appreciably with the increase in density. This is because Mg and K salt does not precipitate out below 29^0 Be'. The concentration of Ca falls with rise in density and remains almost constant from 26.5^0 Be' to 29^0 Be' Bittern. In this study of artificial desalination the 29^{0}Be' bittern shows the negligible concentration of calcium. This is due to the fact that solid fractions of calcium carbonate and calcium sulphate separated between 10-17^0 Be' and 17-24^0 Be' density, respectively and common salt within the density range of 24-29^0 Be' during solar evaporation or artificial desalination. This is due to very long residence times of sodium and chlorine in sea water, while calcium (vital for carbonate formation) tends to precipitate much more quickly [12]. This is further supported by Anthoni J.F. that sea salt can be made by evaporating sea water, may be artificially or naturally[13]. Major amount of sodium chloride is removed within density of 29^0 Be' and some percentage of sodium chloride is carried away with the waste liquor bittern showing higher concentration than 26.5^0 Be'. This may be due to the presence of $MgCl_2$, KCl and other chloride bearing cations present in the bittern. Similarly, SO_4^{2-} anion although is removed as calcium sulphate in the process of evaporation, the SO_4^{2-} content is also enriched. This may be attributed due to the presence of magnesium and potassium as magnesium and potassium sulphate in the system. Several reports have been appeared on this aspect of utilisation and extraction of valued chemicals from sea water [14].

Table 2 : Major elements (gms/lit) in brine and bittern

Major Elements	Brine 2^0 Be'	26.5^0 Be' Bittern	29^{0}Be' Bittern
Mg	1.223	30.633	49.607
Ca	0.28	0.130	0.100
SO_4^{2-}	1.983	42.82	64.70
Cl^-	18.73	185.389	191.979
Na	4.5	73.75	53.75
K	0.1	7.313	10.875

The presence of trace elements in seawater is generally due to the riverine inputs of weathering product of the exposed continent and inputs resulting from the interaction of seawater with oceanic crust. It is observed from the table 3 that the concentration of Co, Cr, Fe, Mn and Sb increases from sea water to 26.5^0 Be' but the concentration is found to be less in 29^0 Be'. Generally, Aluminium occurs as Al^{3+} (aq) under acidic conditions, and as $Al(OH)_4^-$ (aq) under neutral to alkali conditions. Table 3 shows a less concentration of Aluminium in seawater whereas the concentration of Al is not detected in 26.5^0 Be' and 29^0 Be' bittern. Similarly, Silicon which remains as silicic acid in water is found to be 2.9mgs/l in the seawater and remains undetected in bittern.This may be due to co-precipitation with Na and Ca salts. The Boron content in sea brine, bittern and marine by-product was also studied by Dhandhulika & Seshadri[14].Boron occurs as $B(OH)_3$ (aq) or $B(OH)_4^-$ (aq) in seawater. Its concentration varies with a large proportion as compared to the other trace elements. Also the boron concentration is found to be higher than the other mentioned elements in bittern.

Table 3 : Trace elements (mgs/lit) in brine and bittern

Trace Elements	Brine 2^0 Be'	26.5^0 Be' Bittern	29^0Be' Bittern
Al	0.01	nd	nd
B	4.3	37.30	48.49
Co	0.11	4.67	2.65
Cr	0.20	2.01	1.74
Fe	0.20	7.9	7.0
Mn	0.21	0.99	0.68
Ni	0.16	0.03	0.1
Sb	0.0004	7.0	6.0
Si	2.9	nd	nd

Conclusion

Indian Salt industry produced around 15.0 million tonnes of salt every year. Bittern generated in Salt industry contains enriched Potassium and magnesium salts in addition to other important chemicals. Potential recovery of chemicals from bittern in India has not been fully exploited. Considering significance of developing indigenous source of supply for Potash and Magnesia which are important both for the Agricultural and strategic reasons, sea bittern could be utilized to recover potassium and magnesium. There are no viable land based Potash reserves in India but it has seawater, which is a possible source of Potassium salts although in low concentration. With no significant land based source of potash, India imports it's entire requirement of potash. Besides potassium and magnesium, it is also possible to recover sodium chloride, sodium carbonate, bromine, and other strategic metals and chemicals out of this. But the processing routes have the further disadvantage that large quantities of seawater must be handled. So it is better to extract these salts from the bittern for which analysis of bittern plays the major role. In other way this can also simultaneously solve the disposal of such a huge quantity of waste generated at salt field.

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