ABSTRACT

DEVELOPMENT OF A CYCLIC PROCESS FOR THE PRODUCTION OF HIGH PURITY SODA ASH WITH REDUCED FLUORIDE CONTENT FROM MINERAL TRONA

The present invention relates to a development of a cyclical process for the production of soda ash from the mineral trona. More specifically, it relates to production of high purity soda ash with reduced fluoride content from trona available in Magadi lake.

FIELD OF THE INVENTION

The present invention relates to a development of a cyclical process for the production of soda ash from the mineral trona. More specifically, it relates to production of high purity soda ash with reduced fluoride content from trona available in Magadi lake.

BACKGROUND OF INVENTION

Soda ash is one of the most useful inorganic alkali chemicals. It has tremendous application and hence assumes great commercial importance. It is produced commercially using sodium chloride employing Solvay ammonia process. It is also obtained from the naturally occurring mineral trona which is sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$). Trona deposits are found and used in USA and Africa-Kenya. The deposits found in Kenya-Magadi-are surface deposits in Lake Magadi. The typical composition as analyzed, of the Trona found in lake Magadi is given as under.

Constituent	Percent
Na_2CO_3	46
$NaHCO_3$	34
NaF	1.55
NaCl	1.68
Na_2SO_4	0.15
Water insolubles	1.3
H_2O	15.4

The soluble impurity such as sodium fluoride, sodium chloride and sodium sulphate are required to be removed for some of the desired application of soda ash.

Reference may be made to US Patent No. 1 502 850 granted to Allied Chemical Corporation, USA, on "Purification of sodium carbonate" wherein the process has been described to purify the trona available in places such as Magadi Lake and having typical composition as detailed above mainly containing sodium fluoride and insoluble impurities. The process comprises of crystallization of sodium carbonate monohydrate from the interaction between anhydrous soda ash and saturated solution of soda ash above 33 °C and sodium fluoride remains insoluble which is finer in size and is separated from sodium carbonate monohydrate by physical separation employing elutriation. The process suffers the

drawback of sharp separation of sodium fluoride and sodium carbonate monohydrate which is evidenced by the example sited and could contain soda ash with fluoride content of as high as 0.4%.

Reference may be made to US Patent No. 4,021,525 wherein a process of calcinations of trona with additives such as aluminium oxide or bauxite is described mainly to reduce soluble silicates and carbonaceous matter. The process neither describes the removal of soluble impurities such as fluoride and other contaminants nor about the overall purity of the soda ash so produced.

Reference may be made to US Patent No. 3, 980,754 wherein it is disclosed to remove fluoride impurities from natural soda by treatment of solution of calcined natural soda ash with magnesium bicarbonate. The process employs many unit operations including preparation of magnesium bicarbonate. Even though the fluoride concentration is shown to have reduced, the contamination with Mg is the treated solution is increased which is undesirable as shown in US Patent No. 5,783,159 on inorganic impurities removal in soda ash solutions with carbon which deals with removal of Ca and Mg impurities in soda ash solutions.

Reference may be made to PCT bearing international publication number WO 2010/046916 A1, by Sensarma S., and Shastry M., where in use of calcium and magnesium salts is described to precipitate out fluoride as Ca and Mg salts. No mention is made to the extent of fluoride content reduced in the soda ash so prepared and the process suffers from the drawback of possible contamination with Ca and Mg. The process describes the preparation of sodium bicarbonate for specific application qualitatively.

Reference may be made to US 2009/0238740 A1, by Sensarma et al., wherein the method of preparing sodium bicarbonate from trona with reduced fluoride content is described. The process described is silent on remaining trona solution after recovery of bicarbonate and the recovery is very low making the whole process expensive.

OBJECTIVE OF THE INVENTION

The main object of the present invention is to develop a cyclic process for the production of soda ash from trona with reduced impurities.

Another object of the present invention is to reduce fluoride content in the soda ash produced from trona.

Yet another object of the present invention is to reduce the inputs to the process to make it cost effective.

Yet another object of the process is to obtain higher yield of the soda ash from trona.

Yet another object of the present invention is to recycle the solution to achieve high yields reduce the effluent to make the process environmentally friendly

Yet another object of the present invention is to use the carbon dioxide generated in the process of conversion of bicarbonate to carbonate.

SUMMARY OF THE PRESENT INVENTION

In the present invention, a cyclic process has been developed to produce soda ash from trona such as available in lake Magadi which has low fluoride content and exhibits purity exceeding 99.5%. The trona is calcined and dissolved in the recycle liquor, filtered and the solution so obtained is carbonated using the carbon dioxide generated during conversion of sodium bicarbonate to sodium carbonate and carbon dioxide obtained from the dryer of sodium bicarbonate). The bicarbonate so formed is filtered, washed and calcined to obtain soda ash of high purity.

Accordingly, the present invention provides a cyclic process to produce soda ash having higher purity and reduced fluoride content from trona that comprises of i) calcining trona, ii) dissolving trona in recycle solution obtained in step (v), iii) filtering the solution, iv) carbonating the filtrate with carbon dioxide generated in step (vi), v) Filtering the bicarbonate formed in step (iv) and recycling the filtrate to step (ii), vi) drying bicarbonate at 150 °C using indirect heating,

In an embodiment of the present invention, the trona is calcined in the temperature range of 450-500 °C.

In an another embodiment of the present invention, the calcined trona is dissolved in the recycle liquor

In yet another embodiment of the present invention, the solution of trona is filtered using known filtration equipment to reduce insoluble

In yet another embodiment of the present invention, the filtered solution of trona is subjected to carbonation in the carbonation tower

In yet another embodiment of the present invention, the carbon dioxide used for carbonation of the trona solution is obtained from the dryer of sodium bicarbonate

In yet another embodiment of the present invention, sodium bicarbonate formed by carbonation of trona solution is filtered and the filtrate is recycled for dissolution of trona

In yet another embodiment of the present invention, the sodium bicarbonate is dried at 150-160^{0}C by indirect heating and the carbon dioxide formed is used in the carbonation of trona solution

DETAILED DESCRIPTION OF THE INVENTION

The trona containing soluble and insoluble impurities as given by the following typical composition, such as available in lake Magadi is used to produce soda ash having low impurity profile especially with respect to fluoride.

Constituent	Percent
Na_2CO_3	46
$NaHCO_3$	34
NaF	1.55
NaCl	1.68
Na_2SO_4	0.15
Water insolubles	1.3
H_2O	15.4

The cyclic process developed goes through simple unit operations like calcinations, dissolution in the recycle liquor, filtration, carbonation, filtration and drying. The carbonation is carried out using the carbon dioxide generated during drying step. The filtrate obtained after carbonation is recycled in the process. The flow diagram given in Figure-1 explains the applicability of the process.

The inventive steps in the present invention are the step of calcinations that is found very necessary to remove some of the impurities such as organic impurity. If one does not follow this, the product looks apparently white but on dissolution of the final product in water, it gives turbid color. Further, by following this step, the yield increases as all the bicarbonate also goes into solution. If one does not follow calcinations, the cycles can run and the

product yield will reduce but the fluoride reduction can be obtained. The another inventive step is the recycle of the liquor after separation of sodium bicarbonate formed. The cycles are repeated with the small amount of bleed that starts after ten cycles to get consistent product in terms of its impurity profile. The another inventive step is the use of carbon dioxide generated during the drying of bicarbonate to make soda ash in carbonation of the cyclic solution. There is no emission of carbon dioxide into the atmosphere making the process green.

The following examples are given by way of illustration and therefore should not be construed to limit the scope of the present invention.

EAXMPLE-1

15 kg of trona from Magadi was calcined at 500 °C for two hours mainly to reduce organic contamination of the trona. Incidentally, all the sodium bicarbonate got converted to sodium carbonate. The analysis of the raw trona before the calcinations and the after calcinations is given below.

Analysis of raw trona before calcinations

Constituent	Percent
Na_2CO_3	46
$NaHCO_3$	34
NaF	1.55
NaCl	1.68
Na_2SO_4	0.15
Water insolubles	1.8
H_2O	15.4

Analysis of trona after calcination

Constituent	Percent
Na_2CO_3	94.5
$NaHCO_3$	-
NaF	2.15
NaCl	2.33
Na_2SO_4	0.001
Water insolubles	2.6
H_2O	-

The calcined trona obtained weighed, the weight loss during the calcinations is 10.8 kg.

EXAMPLE-2

2 kg of calcined trona produced in EXAMPLE-1 was taken in a cylindrical SS vessel equipped with stirrer to which 10L of water was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 60 gm having following composition.

Na_2CO_3 - 9.75%
$NaHCO_3$ - 5.38%
F^- - 9%
NaCl - 0.59%

The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and washed with water to make filtrate 10L. The solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.7 kg and its composition is as under.

Na_2CO_3 - 99.5%
F^- - 0.09%
NaCl - 0.34%

The filtrate measured 10L and exhibited the following composition.

Na_2CO_3 - 7.2%
$NaHCO_3$ - 6.0%
F^- - 0.17%
NaCl - 0.36%

EXAMPLE-3

10L Of filtrate produced in EXAMPLE-2 was taken in a cylindrical SS vessel equipped with stirrer to which 1 kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 35 gm having following composition.

Na_2CO_3 - 25.4%
$NaHCO_3$ - 10.1%
F^- - 12.5%
NaCl - 2.1%

The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is

around 7.5. The resultant slurry is filtered and washed to make the total quantity of filtrate 10L. The solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.71 kg and its composition is as under.

Na_2CO_3 - 99.6%
F^- - 0.07%
NaCl - 0.36%
The filtrate measured 10L and exhibited the following composition.

Na_2CO_3 - 9.3%
$NaHCO_3$ –5.7%
F^- - 0.19%
NaCl - 0.23%

EXAMPLE-4

10L of filtrate produced in EXAMPLE-3 was taken in a cylindrical SS vessel equipped with stirrer to which 0.8 kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 15 gm having following composition.

Na_2CO_3 - 24.2%
$NaHCO_3$- 7.06%
F^- - 16.5%
NaCl - 1.8%
The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and the solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.98 kg and its composition is as under.

Na_2CO_3 - 98.8%
F^- - 0.07%
NaCl - 0.18 %
The filtrate plus wahing measured 10L and exhibited the following composition.

Na_2CO_3 - 4.2%
$NaHCO_3$ -8.06%
F^- - 0.25 %
NaCl - 0.41%

EXAMPLE-5

10L of filtrate produced in EXAMPLE-4 was taken in a cylindrical SS vessel equipped with stirrer to which 1 kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15

minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 15 gm having following composition.

Na_2CO_3 - 24.2%
$NaHCO_3$- 7.06%
F^- - 12.5%
NaCl - 0.41%

The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and the solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.81 kg and its composition is as under.

Na_2CO_3 - 99.2%
F^- - 0.09%
NaCl - 0.18 %

The filtrate plus washing measured 10L and exhibited the following composition.

Na_2CO_3 - 3.5%

$NaHCO_3$ -8.0%

F^- - 0.25 %
NaCl - 0.36%

EXAMPLE-6

10L of filtrate produced in EXAMPLE-3 was taken in a cylindrical SS vessel equipped with stirrer to which 0.9 kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 76 gm having following composition.

Na_2CO_3 - 47.5%
$NaHCO_3$- 8.06%
F^- - 7.5%
NaCl - 0.41%

The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and the solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.65 kg and its composition is as under.

Na_2CO_3 - 99.64%
F^- - 0.06%
NaCl - 0.18 %
The filtrate plus washing measured 10L and exhibited the following composition.

Na_2CO_3 - 3.39%
$NaHCO_3$ -8.06%
F^- - 0.19 %
NaCl - 0.35%

EXAMPLE-7

10L of filtrate produced in EXAMPLE-3 was taken in a cylindrical SS vessel equipped with stirrer to which 1kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 30 gm having following composition.

Na_2CO_3 - 33.9%
$NaHCO_3$- 5.03%
F^- - 16.5%
NaCl - 1.8%
The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and the solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.9 kg and its composition is as under.

Na_2CO_3 - 99.6%

F^- - 0.07%
NaCl - 0.23 %
The filtrate plus wahing measured 10L and exhibited the following composition.

Na_2CO_3 - 4.0%
$NaHCO_3$ -6.0%
F^- - 0.2 %
NaCl - 0.36%

EXAMPLE-8

10L of filtrate produced in EXAMPLE-3 was taken in a cylindrical SS vessel equipped with stirrer to which 0.75 kg of calcined trona prepared in EXAMPLE-1 was added and stirred for 15 minutes to dissolve the material. The solution was filtered using vacuum filter to remove insolubles. The residues remained after filtration weighs 29 gm having following composition.

Na_2CO_3 - 25.4%
$NaHCO_3$- 6.4%
F^- - 6.5%
NaCl - 0.64%

The clear solution was heated to 80 °C and subjected to carbonation under hot condition for about one hour to convert sodium carbonate to bicarbonate till the pH of the solution is around 7.5. The resultant slurry is filtered and the solids are dried at 150 °C to convert sodium bicarbonate to sodium carbonate. The weight of sodium carbonate obtained is 0.64 kg and its composition is as under.

Na_2CO_3 - 99.2%
F^- - 0.092
NaCl - 0.18 %

The filtrate plus wahing measured 10L and exhibited the following composition.

Na_2CO_3 - 3.0%
$NaHCO_3$ -8.06%
F^- - 0.28 %
NaCl - 0.41%

The above cycles can also be carried out with trona as such without using calcined trona but with reduced overall yield as exemplified in the following examples, 9,10 and 11.

EXAMPLE-9

6 kg of raw trona is taken in 10L of water and stirred to make saturated solution. The solution is filtered to remove insolubles. The clear filtrate was subjected to carbonation till the pH of the solution is 7.5. The slurry obtained is filtered and washed to make total filtrate 10L; and the solids were dried at 150 °C to convert sodium bicarbonate to carbonate. 0.9 kg of dry sodium carbonate was obtained having following specification.

Na_2CO_3 - 98%
F^- - 0.19%
NaCl - 0.69 %

6 kg of raw trona is taken in 10L of water and stirred to make saturated solution. The solution is filtered to remove insolubles. The clear filtrate was subjected to carbonation till the pH of the solution is 7.5. The slurry obtained is filtered and washed to make total filtrate 10L; and the solids were dried at 150 °C to convert sodium bicarbonate to carbonate. 0.9 kg of dry sodium carbonate was obtained having following specification.

Na_2CO_3 - 98%
F^- - 0.19%
NaCl - 0.69 %

EXAMPLE-10

5 kg of raw trona is taken in 10L of filtrate obtained in EXAMPLE-9 and stirred to make saturated solution. The solution is filtered to remove insolubles. The clear filtrate was subjected to carbonation till the pH of the solution is 7.5. The slurry obtained is filtered and washed to make total filtrate 10L; and the solids were dried at 150 °C to convert sodium bicarbonate to carbonate. 0.8 kg of dry sodium carbonate was obtained having following specification.

Na_2CO_3 - 98.8%
F^- - 0.18%
NaCl - 0.69 %

EXAMPLE-11

3 kg of raw trona is taken in 10L of water and stirred to make saturated solution. The solution is filtered to remove insolubles. The clear filtrate was subjected to carbonation till the pH of the solution is 7.5. The slurry obtained is filtered and washed to make total filtrate 10L; and the solids were dried at 150 °C to convert sodium bicarbonate to carbonate. 0.7 kg of dry sodium carbonate was obtained having following specification.

Na_2CO_3 - 99.2%
F^- - 0.0.07 %
NaCl - 0.69 %

The above examples indicates that the yield of the soda ash obtained is reduced if calcination of the trona is not carried out, but the reduction of fluoride in the product is attained.

A process for recovery of high purity soda as with reduced fluoride content from trona that comprises: (i) i) calcining trona, ii)dissolving trona in recycle solution obtained in step (v), iii)filtering the solution, iv)carbonating the filtrate with carbon dioxide generated in step (vi), v)Filtering the bicarbonate formed in step(iv) and recycling the filtrate to step (ii), vi) drying bicarbonate at 150 °C using indirect heating.

The trona is calcined in the temperature range of 450-500 °C for 2 hrs.

The calcined trona is dissolved in the recycle liquor.

The solution of trona is filtered using known filtration equipment to reduce insoluble.

The filtered solution of trona is subjected to carbonation in the carbonation tower.

The carbon dioxide used for carbonation of the trona solution is obtained from the dryer of sodium bicarbonate and calcinations of trona.

Sodium bicarbonate formed by carbonation of trona solution is filtered and the filtrate is recycled for dissolution of trona.

The sodium bicarbonate is dried at 150-160 °C by indirect heating and the carbon dioxide formed is used in the carbonation of trona solution.

The process can also be operated without calcining the trona and using raw trona as such but with reduced yield (15-23 %).

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