

A PROCESS FOR REDUCING SODIUM FLUORIDE CONTENT IN TRONA OR SODA ASH

Technical Field

The disclosure relates to a process for reduction of fluoride impurities from trona or soda ash. Specifically, it relates to a process for reduction of sodium fluoride from trona or soda ash.

Background

Trona is a mineral comprising sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). It is found in a number of deposits around the world, for example, in Wyoming (USA), Magadi (Kenya), Tanzania (Lake Natron), Turkey, Venezuela and Egypt.

Trona is generally used for the manufacture of soda ash by well-established techniques which generally include milling the trona, which has either been mined or dredged depending on the location of the trona deposit, and calcining the milled trona to produce soda ash. Soda ash thus produced, generally incorporates a few impurities that were present in the original trona deposit. Therefore, soda ash derived from trona is less pure than soda ash obtained from a synthetic process. Various processes have been proposed for purifying soda ash derived from trona.

The trona deposits found in Africa, particularly at Magadi (Kenya) incorporate sodium fluoride as barnacle-like encrustations on the trona crystals. The encrustations have a large numbers of small individual crystals of sodium fluoride. The encrustations degrade into their constituent crystals during the initial milling of trona. Soda ash produced from such trona contains sodium fluoride at a level of 0.5% to 3%, and more typically 1% to 1.5% by weight.

Some uses of soda ash such as steel and glass making involve high temperatures. In such cases, the presence of sodium fluoride in soda ash gives rise to fluoride containing emissions that are undesirable from an environmental viewpoint.

Several processes have been proposed to remove sodium fluoride from trona or soda ash produced therefrom. One such process utilizes different solubility of sodium fluoride

and trona or soda ash in water. The process involves preferential re-crystallization of soda ash after dissolving it in fresh water followed by solid-liquid separation and calcining. However, the process leads to incomplete removal of sodium fluoride. Also, the extent of sodium fluoride removed varies with sodium fluoride content in original trona or soda ash.

US patent 3,980,754 discloses a process for purification of an alkali carbonate containing a fluoride impurity. The process comprises dissolving crude alkali carbonate in an aqueous solution or suspension of magnesium bicarbonate in order to transfer the fluoride impurity into the resulting colloidal flocculated precipitate without formation of magnesium fluoride. The process results in a partial removal of sodium fluoride. Further, a significant amount of sodium carbonate and sodium bicarbonate get converted to insoluble calcium carbonate and/or magnesium carbonate resulting in loss of sodium bicarbonate.

WO 2010/046916 A1 discloses a process for reducing fluoride impurities in crude trona. The process comprises preparing an aqueous solution of crude trona, adding to the aqueous solution of crude trona a calcium or magnesium salt to precipitate fluoride impurities as calcium or magnesium fluoride, and separating the precipitated fluoride impurities from the trona solution to obtain a trona solution with reduced fluoride impurities. This process does not remove fluoride impurities completely. Further, the disclosed process is energy intensive.

The processes known in the art are either energy intensive and/or do not completely remove sodium fluoride from trona or soda ash produced from trona. Additionally, the impurities including sodium fluoride separated from the soda ash or trona are pushed back into trona lake or deposits. This not only affects the environment but also increases the content of such impurities in trona deposits further.

Thus, there is a need for a process for removing sodium fluoride from trona or soda ash such that the final product has no or insignificant levels of sodium fluoride. Further, such process should be energy efficient and environment friendly.

Detailed Description

To promote an understanding of the principles of the invention, reference will be made to the embodiments and specific language will be used to describe the same. It will

nevertheless be understood that no limitation of scope of the invention is thereby intended, such alterations and further modifications in the illustrated methods and such further applications of the principles of the inventions as described therein being contemplated as would normally occur to one skilled in art to which the invention relates.

It will be understood by those skilled in the art that the foregoing general description and the following detailed description are exemplary and explanatory of the invention and are not intended to be restrictive thereof.

The disclosure relates to a process for reducing the content of sodium fluoride in trona or soda ash. The process comprises mixing the trona or the soda ash with saline water to precipitate the sodium fluoride present in the trona or the soda ash, and separating the precipitated sodium fluoride from the mixture to obtain a trona or soda ash solution having reduced sodium fluoride content. The saline water comprises sodium chloride in a range of 1 to 10% by weight to precipitate the sodium fluoride present in the trona or the soda ash. The trona or soda ash solution obtained after the precipitation of the sodium fluoride contains less than 10% sodium fluoride present in the trona or the soda ash.

In an example, the sodium chloride in the saline water is in the range of 2% to 10% by weight. In another example, the sodium chloride in the saline water is in the range of 3% to 5% by weight. The presence of sodium chloride in the saline water significantly decreases the solubility of sodium fluoride resulting in precipitation of the latter.

In an embodiment, the saline water is obtained from a natural salt water body. Examples of the natural salt body include sea water and salt lake water. The seawater comprises three major cations which are Na^+ , Mg^{2+} and Ca^{2+} . During the process, Mg^{2+} and Ca^{2+} cations may undergo a reaction with some of the sodium fluoride present in the trona or soda ash forming magnesium fluoride or calcium fluoride respectively.

Temperature of the mixture is between 20°C and 60°C. In an embodiment, the temperature is in the range of 30°C to 50°C.

pH of the mixture is between pH of the mixture is between 8 and 12. In an embodiment, the pH is in the range of 9 to 11.

Any conventional method of solid-liquid separation can be used to separate the precipitated sodium fluoride from the mixture. Examples of such method include but not limited to filtration, centrifugation and decantation.

In accordance with an embodiment, the trona or soda ash solution is subjected to crystallization or precipitation. The crystallized or precipitated trona or soda ash is then separated by any conventional method as mentioned above and then dried. The concentration of sodium fluoride in the crystals or the precipitate of trona or soda ash is less than 0.05% by weight. In an embodiment, the concentration is less than 0.03%.

In accordance with an embodiment, the trona solution obtained after separating the precipitated sodium fluoride is used directly for preparation of sodium carbonate or soda ash by any known method. The concentration of sodium fluoride in the soda ash prepared from the trona solution is less than 0.05% by weight. In an embodiment, the concentration is less than 0.03%.

The trona can be milled before mixing it with the saline water. The solution obtained after the crystallization of trona or soda ash may be recycled by adding it to a new mixture of saline water and trona or soda ash.

The disclosed process is further illustrated through following examples which are for illustrative purpose only and should not be construed to limit the scope of the present invention.

Examples

Example 1: 100 grams (g) trona containing 2.2 % by weight sodium fluoride along with 1.0% by weight water insoluble compounds like silica was mixed in sea water containing 3% by weight sodium chloride under stirring. The insoluble part was separated from liquid by filtration and washing with the saline water. The resultant liquid was then subjected to crystallization by cooling the solution to a desired temperature for crystallization. The crystals were recovered by filtration under vacuum and dried. The solid thus recovered exhibited purity level of more than 99%. The fluoride concentration was measured by ion-selective electrode method and was found to be 20 ppm.

Example 2: 100 g soda ash derived from Magadi trona and containing 3.5% by weight sodium fluoride was mixed with 300 g sea water containing 3.5% by weight sodium chloride under stirring. The purified soda ash was obtained following the same process mentioned Example 1. The sodium fluoride concentration was measured by ion-selective electrode method and was found to be 34 ppm.

Example 3 to 8: X kg Trona containing Y % sodium fluoride as main impurity was mixed in Z kg sea water under stirring. The sea water contains about 3% sodium chloride by weight. The insoluble part was separated from liquid by using conventional solid liquid separation methods and optionally washing with the saline water. The resultant liquid was then subjected to crystallization by cooling the solution to a desired temperature for crystallization. The crystals were recovered by using conventional solid liquid separation and dried. The filtrate thus obtained can optionally be recycled by topping up required quantity of the fresh Trona and sea water and repeat the above-mentioned process in a continuous or a batch process.

The purified solid thus recovered exhibited sodium carbonate purity level in the range of > 98%. The sodium fluoride concentration was measured by ion-selective electrode method and was <0.05%. The results of various experiments are illustrative in Table 1.

Table 1: Illustrative Examples

Example	Trona (X), Kg	NaF (Y), %	Sea water (Z), Kg
3	1.0	0.5	2.5
4	1.0	2.0	3.0
5	1.0	4.0	5.0
6	0.6	2.0	1.0
7	0.6	2.0	1.0
8	0.6	2.0	1.0

Example 7 to 12: X kg Soda ash obtained from Magadi Trona containing Y % sodium fluoride as main impurity was mixed in Z kg sea water under stirring. The sea water contains about 3% sodium chloride by weight. The insoluble part was separated from liquid by using

conventional solid liquid separation methods and optionally washing with the saline water. The resultant liquid was then subjected to crystallization by cooling the solution to a desired temperature for crystallization. The crystals were recovered by using conventional solid liquid separation and dried. The filtrate thus obtained can optionally be recycled by topping up required quantity of the fresh Soda ash and sea water and repeat the above-mentioned process in a continuous or a batch process.

The purified solid thus recovered exhibited sodium carbonate purity level in the range of > 98%. The sodium fluoride concentration was measured by ion-selective electrode method and was <0.05%. The results of various experiments are illustrative in Table 2.

Table 2: Illustrative Examples

Example	Soda Ash obtained from Trona (X), Kg	NaF (Y), %	Sea water (Z), Kg
9	1.0	0.5	2.0
10	1.0	3.0	2.5
11	1.0	5.0	4.0
12	0.8	3.0	2.0
13	0.8	3.0	2.0
14	0.8	3.0	2.0

Industrial Applicability

The disclosed process is simple and energy efficient. The process allows for the reduction of fluoride impurities to an amount less than 0.05% by weight. In an embodiment, the purified trona or soda ash contains less than 0.03% sodium fluoride by weight.

Soda ash or sodium carbonate obtained using the disclosed process can be used in high end application such as food and pharmaceuticals due to absence or insignificant concentration of sodium fluoride in the same.

The process is environment friendly and economical.

Claim:

1. A process for reducing sodium fluoride content in trona or soda ash, comprising:
 - a.) mixing the trona or the soda ash with saline water comprising sodium chloride in a range of 1 to 10% by weight to precipitate the sodium fluoride present in the trona or the soda ash; and
 - b.) separating the precipitated sodium fluoride from the mixture to obtain a trona or soda ash solution having reduced sodium fluoride content.
2. The process as claimed in claim 1 further comprising subjecting the trona or soda ash solution to crystallization to obtain crystals of purified trona or soda ash.
3. The process as claimed in claims 2, wherein the crystals of purified trona or soda ash contain less than 0.05% sodium fluoride by weight.
4. The process as claimed in claim 1 further comprising preparing soda ash directly from the trona solution.
5. The process as claimed in claims 4, wherein the soda ash prepared directly from the trona solution contains less than 0.05% sodium fluoride by weight.
6. The process as claimed in claim 1 further comprising milling the trona before mixing it with the saline water.
7. The process as claimed in claim 1 further comprising recycling solution obtained after the crystallization by adding it to a new mixture of saline water and trona or soda ash.
8. The process as claimed in claim 1, wherein the saline water is sea water.
9. The process as claimed in claim 1, wherein temperature of the mixture is in a range of 20 °C to 60 °C.
10. The process as claimed in claim 1, wherein pH of the mixture is in a range of 8 to 12.

11. The process as claimed in claim 1, wherein the sodium chloride in the saline water is in the range of 2% to 10% by weight.
12. The process as claimed in claim 1, wherein the sodium chloride in the saline water is in the range of 3% to 5% by weight.