

PROCESS FOR FORMING CALCIUM NITRITE

Production of aqueous calcium nitrite solutions by absorbing nitrogen oxide gases in a basic calcium hydroxide solution has been known for some time. Such solutions can be employed as additives in cement formulations.

5 Thus Chemical Abstracts, volume 77 (1972) abstracting an article from Ref Zh, Khim 1971, describes the use of milk of lime to trap waste gases from production of nitric acid. CA85:145344e discloses mixing nitrogen oxide gases with a slurry of calcium hydroxide to form an aqueous solution of calcium nitrite.

10 CA84:61959 discloses absorbing nitrogen oxide gases in a calcium hydroxide slurry which is filtered to give a calcium nitrite solution. The abstract of a journal article appearing in Zh Neorg Khim 1973, 18(12), 3340-1 indicates that anhydrous calcium nitrite can be prepared by the
15 reaction of calcium hydroxide with ammonium nitrite followed by heating the crystallohydrates in a vacuum.

US Patent 1,471,711 describes absorption of nitrogen oxide gases into soda and caustic soda solutions to produce aqueous nitrite solutions. US Patent 2,797,144 describes a
20 process for producing ammonium nitrite wherein nitrogen oxide gases with an NO/NO₂ molar ratio of at least 4 are contacted with oxygen and ammonium carbonate or ammonium sulfite. In USP 3,928,543 nitrogen oxide gases are contacted with aqueous hydroxide solutions (e.g., calcium hydroxide), and
25 the progressive dilution of the nitrogen oxide content of the

gas is correlated with the base content of the solution. In USP 4,009,246 high temperature gases containing nitrogen oxide are contacted with aqueous solutions of a base (e.g. calcium hydroxide) to rapidly lower the temperature of the gas and produce nitrite salts containing the cation of the base. US Patent 4,045,540 describes production of ammonium nitrite by absorbing gases containing nitrogen oxides into a basic solution containing ammonium cation. Air pollution from residual nitrogen oxide gases is reduced by adding controlled supplemental quantities of NO₂ to the absorption system. US Patent 4,053,555 describes a system for scrubbing industrial waste gases containing nitrogen oxides with an aqueous solution to absorb the gases. Subsequently, "desorption" is accomplished to regenerate the initial scrubbing solution, which can be recirculated.

This invention provides a process for preparing aqueous solutions of calcium-nitrite which comprises:

- (a) forming an aqueous solution of sodium nitrite and calcium nitrate,
- (b) cooling said solution to insolubilize sodium nitrate and form an aqueous solution of calcium nitrite; and
- (c) separating the aqueous calcium nitrite solution from the insoluble sodium nitrate.

Thus the invention comprises first forming a solution of sodium nitrite and calcium nitrate in water. The solution is cooled to insolubilize sodium nitrate, which is separated

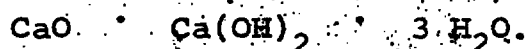
from the residual aqueous solution of calcium nitrite. Preferably thereafter, calcium hydroxide is mixed with the calcium nitrite solution to form a calcium nitrite/calcium hydroxide double salt. The solution is cooled to insolubilize the double salt, which is then separated. Subsequently, the double salt is dissolved in water to form calcium hydroxide (insoluble) and an aqueous solution of calcium nitrite. The insolubilized calcium hydroxide is separated and can be recycled to form additional amounts of the double salt. Also, the calcium nitrite solution from which the double salt precipitates can be recycled into contact with the initial sodium nitrite/calcium nitrate solution.

The present invention is based upon several unexpected findings. First, as the initial sodium nitrite/calcium nitrate solution is cooled, it is unexpected that sodium nitrate will precipitate. Also, it is unexpected that substantial precipitation will occur within relatively narrow temperature swings, e.g., 20 to 30 Centigrade degrees. These discoveries therefore provide a convenient method for separating substantial amounts of sodium and nitrate ions from the reaction mixture, which contributes significantly to the purity of the final calcium nitrite solution.

Secondly, the invention utilizes the formation of a double salt of calcium nitrite with calcium hydroxide. Numerous processes described in the literature attempt to avoid double salt formation. However, in the present

invention a double salt is deliberately formed to provide a second method of separating calcium nitrite from residual impurities which remain in solution. The double salt employed in the present invention is believed to have the formula

$\text{Ca}(\text{NO}_2)_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}$, although the formula has also been described as



In forming the sodium nitrite/calcium nitrate solution, the molar $\text{NaNO}_2/\text{Ca}(\text{NO}_3)_2$ ratio is desirably from 1.9 to 2.2, and generally is about 2. The solution can be formed by simply dissolving the salts in water or, alternatively, separate solutions of each salt can be formed and the solutions mixed. Also, it is possible to form a solution of one of the salts and add the second salt thereto. To provide adequate solubility, the solution is generally formed at a temperature of 70 to 110°C. The aqueous solution is generally concentrated with regard to both salts, although the concentrations on a weight percentage basis are suitably from 30 to 40 for (anhydrous) calcium nitrate and from 30 to 40 for sodium nitrite.

Following formation, the solution is cooled to a temperature of, say, 0 to 30°C, and preferably 15 to 30°C. As the temperature is lowered, the sodium nitrate will precipitate. It has been noted that calcium nitrite also tends to precipitate to a small degree, especially at temperatures below about 10°C, assuming that a saturated solution is employed.

The insoluble sodium nitrate is separated to provide an aqueous phase enriched in calcium nitrite, although both sodium and nitrate ions remain behind. Generally, the residual concentration in the aqueous phase of sodium nitrate and sodium nitrite, in the form of their respective ions, will be up to 10% for sodium nitrate and up to 8% for sodium nitrite.

As described above, the residual calcium nitrite solution is contacted with calcium hydroxide to form the double salt. The calcium hydroxide is generally employed in the form of slaked lime or an equivalent thereof, e.g. burnt lime. Generally the aqueous solution is heated to a temperature of from 50 to 90°C prior to addition of the calcium hydroxide. It has been discovered at temperatures below about 55°C, formation of a "gel" tends to occur wherein needle-like crystals rapidly form a haze in the solution, which prevents adequate stirring. To obviate gel formation, the solution can be heated or else the calcium hydroxide can be added at a higher temperature.

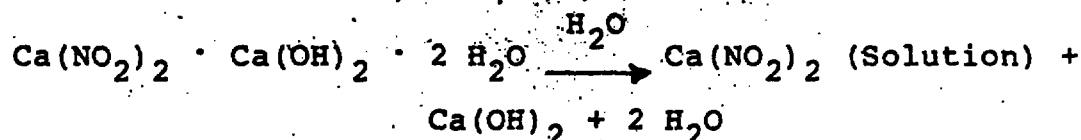
The amount of calcium hydroxide employed depends upon a number of factors. The function of the calcium hydroxide is essentially as a carrier for calcium nitrite, i.e., the calcium hydroxide forms the insolubilized double salt which can be utilized to separate portions of the calcium nitrite from the solution. Thereafter the double salt is dissolved to liberate the calcium nitrite and regenerate the calcium hydroxide. Therefore it is apparent that the amount of calcium hydroxide used should be sufficient to produce the maximum amount of double salt possible,

bearing in mind the stoichiometry and temperature equilibria discussed below. With regard to the formation of the double salt and subsequent dissolution to liberate the calcium nitrite, the reactive stoichiometry is believed to be as follows:

I. Precipitation of Double Salt;



II. Liberation of Calcium Nitrite;



- 10 In aqueous solutions wherein both calcium hydroxide and calcium nitrite are present, the calcium nitrite is in equilibrium with the insoluble double salt. For example, at 20°C, and assuming that the solution is saturated with respect to calcium
- 15 hydroxide and calcium nitrite, the maximum concentration of calcium nitrite in solution will be 20 weight percent, with the remainder being present as the insoluble double salt. At 30°C the maximum is 22.5%. Above about 55°C double salt formation fails to occur,
- 20 thus the formation of the double salt should proceed at less than about 55°C. The calcium hydroxide should be added in an amount sufficient to form as much of the double salt as possible. For example, at 20°C, if the calcium nitrite solution has a concentration of 35%,
- 25 enough calcium hydroxide should be added to convert 3/7 of the calcium nitrite to the double salt. This will reduce the concentration of calcium nitrite to 20%, with the remainder as double salt based on the equilibrium discussed above and the stoichiometry of the first
- 30 equation. If excess calcium hydroxide is added, this

will not result in formation of more double salt. If insufficient calcium hydroxide is added, the amount of double salt formed will not be maximized and this detracts from the efficiency of the process. For any
5 given temperature within the range of 0°C to 55°C, the equilibrium between the double salt and calcium nitrite can easily be determined by cooling a solution saturated with respect to calcium hydroxide and calcium nitrite but containing excess calcium nitrite,
10 to the desired temperature and measuring the amounts of double salt formed and the amount of calcium nitrite remaining in solution. The amount of calcium hydroxide can then be adjusted accordingly.

Following formation, the double salt is separated
15 from the aqueous phase and dissolved in water to produce a solution of calcium nitrite and precipitate calcium hydroxide. The concentration of calcium nitrite can be determined according to the stoichiometry of equation II above. However, the temperature of the
20 solution must be sufficient to dissolve all of the double salt so that the equilibrium discussed above does not interfere. Conveniently, solutions can be prepared with calcium nitrite concentrations of 20-35%, and preferably 27-35%, by weight. Presently,
25 solutions of 30% by weight calcium nitrite are sold for use as corrosion inhibitors in concrete formulations.

The precipitated calcium hydroxide can be separated and reused to form more of the double salt. The amount of impurities in solutions produced during the
30 process measured as sodium nitrite and sodium nitrate will generally not exceed 8% by weight sodium

nitrate and 4% by weight sodium nitrite.

The process of the invention can be carried out on a batch or continuous basis.

The invention will now be illustrated, merely by way of example, with reference to Figure 1 of the accompanying drawings which is a schematic diagram of a batch process of the invention.

In Figure 1, an aqueous solution of calcium nitrate is conveyed into mixing tank 1 fitted with stirring apparatus 3, cooling means 5 and heating means 7.

As discussed above, the aqueous solution is cooled in mixing tank 1 to a temperature of from, 0 to 30°, preferably from 15 to 30°C, thereby causing by-product sodium nitrate to precipitate and exit through the bottom of mixing tank 1 through conduit 9. The heating means 7 is employed to form the initial calcium nitrate/sodium nitrite solution in mixing tank 1. In forming the solution, stirring apparatus 3 is also employed to disperse the salts.

Following precipitation of the sodium nitrate, the enriched calcium nitrite solution is withdrawn from mixing tank 1 through conduit 11 utilizing pump 13 and deposited in tank 15 equipped with stirring means 17, cooling elements 19 and heating means 21. Recycled calcium hydroxide is introduced through conduit 23 into tank 15. Any "make-up" calcium hydroxide necessary to achieve the desired concentration as described above enters through conduit 25. The initial temperature of tank 15 during addition of calcium hydroxide is generally from 60 to 80°. Thereafter, cooling elements 19 (e.g., cooling-water conduits) are activated to lower the

temperature of the calcium hydroxide/calcium nitrite mixture to the desired level, causing precipitation of the double salt which is removed along with the calcium nitrite solution from tank 15 through conduit 27 onto rotary filter 29. Residual calcium nitrite solution emanating from rotary filter 29 is returned through conduit 31 to tank 1. The filtered double salt from rotary filter 29 is conveyed through line 33 to tank 35 fitted with stirring means 37 and heating means (e.g. a steam sparger) 39 and conduit 41. Water enters tank 35 through conduit 41 and is heated to a temperature of from 50 to 90°C (e.g., about 80°C) to solubilize the double salt and precipitate calcium hydroxide. The product slurry containing precipitated calcium hydroxide passes from tank 35 through conduit 43 and line 45 onto a rotary filter 47 where product calcium nitrite solution is separated and flows to storage through line 49, and solid calcium hydroxide is recycled to tank 15 through line 23.

In the following Example, which further illustrates the present invention, all percentages are by weight based on the total weight of the solution, slurry etc, unless otherwise stated.

Example

100 g of NaNO_2 was mixed with a solution of $\text{Ca}(\text{NO}_3)_2$ (171 g of tetrahydrate in 36 g H_2O). The combined solutions had a temperature of about 100°C and were cooled to a temperature of about 20°C to precipitate NaNO_3 . 96.5 grams of the NaNO_3 were collected. The mother liquor was heated to 75°C, and 42 grams of $\text{Ca}(\text{OH})_2$ were added thereto. The admixture was cooled to 25°C to form 209 grams

(147.6 g THEORETICAL) of a double salt having the general formula $\text{Ca}(\text{NO}_2)_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}$.

The precise formula for the double salt may vary, especially in the amount of hydrated water. For the

5 purposes of the present invention, it is important only that the $\text{Ca}(\text{OH})_2$ combine with the $\text{Ca}(\text{NO}_2)_2$ in solution to form an insoluble salt which can be precipitated, thereby affording a means for separating the $\text{Ca}(\text{NO}_2)_2$ from the sodium and nitrate ions
10 contributed by the starting materials.

209 grams of the double salt were washed with 100 grams of water at a temperature of 20°C , and the washed double salt (143.6 g) was dissolved in 72 g H_2O at 75°C , releasing the $\text{Ca}(\text{OH})_2$ and producing
15 124 g of a $\text{Ca}(\text{NO}_2)_2$ solution having a 31.4% concentration.



C L A I M S

1. A process for preparing an aqueous solution of calcium nitrite which comprises:

(a) forming an aqueous solution of sodium nitrite and calcium nitrate,

5 (b) cooling said solution to insolubilize sodium nitrate and form an aqueous solution of calcium nitrite; and

(c) separating the aqueous calcium nitrite solution from the insoluble sodium nitrate.

10 2. A process according to claim 1 wherein the solution of step (b) is maintained at a temperature of from 0 to 30°C to precipitate sodium nitrate.

3. A process according to claim 1 or 2 wherein in step (a) the molar $\text{NaNO}_2/\text{Ca}(\text{NO}_3)_2$ ratio is from 1.9:1
11 to 2.2:1.

4. A process according to any one of the preceding claims wherein the temperature of the solution formed in step (a) is from 70 to 110°C.

5. A process according to any one of the
15 preceding claims wherein in step (b) the aqueous solution is cooled to a temperature of from 15 to 30°C to precipitate sodium nitrate.



6. A process according to any one of the preceding claims which comprises the additional steps of:

(d) mixing calcium hydroxide with the aqueous calcium nitrite solution of step (c);

(e) forming a water-insoluble calcium nitrite/calcium hydroxide double salt and separating said double salt from the aqueous phase;

(f) decomposing the double salt in the presence of water to form insoluble calcium hydroxide and an aqueous solution of calcium nitrite; and

(g) separating the aqueous calcium nitrite solution from the insoluble calcium hydroxide.

7. A process according to claim 6 wherein the aqueous phase formed in step (e) is recycled to step (a).

8. A process according to claim 6 or 7 wherein the calcium hydroxide formed in step (f) is recycled to step (d) to be utilized as all or part of the calcium hydroxide employed in said step (d).

9. A process according to any one of claims 6 to 8 wherein the aqueous solution of calcium nitrite formed in step (f) has a concentration of from 20 to 35 weight percent.

10. A process according to claim 9 wherein the solution concentration is from 27 to 35 weight percent of calcium nitrite.



11. A process according to any one of claims 6 to 10 wherein steps (a) - (g) are carried out on a batch basis.

12. A process according to any one of claims 6 to 10 wherein the steps (a) - (g) are carried out on a continuous basis.

13. A process according to any one of claims 6 to 12 wherein in step (f) the aqueous phase is maintained at a temperature of from 20 to 50°C to form insoluble calcium hydroxide.

14. A process according to claim 1 substantially as described in the Example.

15. An aqueous calcium nitrite solution whenever prepared by a process as claimed in any one of the preceding claims.