

# ALIEN PROPERTY CUSTODIAN

## MANUFACTURE OF NITRATES OF METALS OF THE ALKALINE METAL GROUP

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This invention relates to the manufacture of nitrates of metals of the alkaline metal group and has for its object a process by means of which it is made commercially possible to manufacture the desired nitrates in a solid form from readily available solutions of other nitrates and by the aid of inexpensive solutions of alkali metal salts other than nitrate.

The present application is a continuation in part of my pending application Serial No. 727,832, filed on the 26th of May 1934, which application is a continuation in part of my prior application Serial No. 618,942, dated 23rd of June 1932.

In the manufacture of nitrogen oxygen compounds from atmospheric nitrogen, nitrate solutions are obtained by reacting upon compounds of alkaline or alkaline earth metals with dilute nitrous gases or nitric acid obtained by the absorption of nitrous gases in water. Large quantities of sodium and calcium nitrates in a dry or solid form are produced by evaporation of the nitrate solutions so obtained.

In the conventional manufacture of calcium nitrate from synthetic nitric acid and limestone (or other calcium compounds, such as for example phosphate rock) the raw material is dissolved in a nitric acid of a strength of between 30 and 60 percent. The acid most frequently employed, however, has a strength of between 50 and 55 percent but under certain circumstances acid of a percentage as low as 20 percent is also sometimes employed.

The concentration of the resulting solutions of calcium nitrate will correspond to the concentration of the acid employed and will be between 30 and 60 percent when a nitric acid of between 30 and 60 percent has been employed to dissolve limestone. If the raw material is a dolomite or other limestone containing magnesium carbonate, the solutions will contain a corresponding percentage of magnesium nitrate. If the raw material employed is a phosphate rock the percentage of alkaline earth metal nitrate in the solution, resulting after the removal of phosphoric acid may sometime be as low as about 20 percent.

The sodium nitrate solutions obtained by the absorption of residual dilute nitrous gases in sodium carbonate usually contain about 20-30 percent (most frequently about 22 percent of sodium nitrate).

Sodium, potassium or ammonium nitrate may be obtained from the calcium nitrate solutions above referred to for example by double decomposition with sodium, potassium or ammonium sulphate and subsequent evaporation of the re-

sulting sodium, potassium or ammonium nitrate solution. In such a process large quantities of calcium sulphate (gypsum) are obtained as a by-product, which is of little or no commercial value. In addition, the obtained solutions of alkaline metal nitrates contain small percentages of dissolved gypsum, which complicates the recovery of the solid nitrates by evaporation.

Other methods for the conversion of nitrates of calcium or other metals into a nitrate of a different metal are also known. All of these prior methods, however, involve drawbacks and difficulties of various kinds and are not satisfactory from a commercial point of view, particularly in their application on the nitrate solutions above referred to.

In the process which is the object of the present invention important advantages are obtained as compared with the known process for the conversion of nitrate of one metal into a nitrate of a different metal.

An important feature of the process according to the invention consists in the use of a base-exchanging substance (of the zeolite or permutite type) as a means to bring about the conversion of nitrates contained in solutions of the nature above referred to.

Another important feature of the invention consists in the method of operation according to which three different solutions—viz. a nitrate solution of a considerable degree of concentration, a washing liquid free from substances which would contaminate the products to be obtained, and a regenerating solution of an alkali metal salt other than a nitrate—are passed in continuous sequence and in immediate contact with one another in a downward direction through a comparatively high layer of the base-exchanging substance.

Other important features of the invention will appear from the following description.

The described process is particularly adapted for the manufacture of alkaline metal nitrate but it is applicable also in the manufacture of other metal salts.

An important application of the process according to the invention consists in the manufacture of sodium or potassium nitrate from calcium and/or magnesium nitrate and sodium or potassium chloride.

Another important application of the invention is the manufacture of potassium nitrate from sodium nitrate and potassium chloride or sulphate.

A further application of the process consists in

the conversion of sodium nitrate and ammonium carbonate and sodium or potassium chloride into ammonium nitrate and sodium or potassium carbonate as an intermediate step in the manufacture of sodium or potassium nitrate from nitrous gases and alkaline metal chlorides, as described in my prior application, Serial No. 618,943.

When the invention is employed for the manufacture of sodium nitrate from a calcium nitrate solution, one may for example proceed as follows:

To commence with, one has a calcium nitrate and a sodium chloride solution, also zeolite saturated with sodium salts, in other words, sodium zeolite. The zeolite must be of a quality through which liquids easily penetrate, and must be composed of grains of a suitable size (for example 0.4-0.8 mm diameter). It is placed inside a container that may be a few metres high, and is deposited on a perforated plate or the like. The major part of the space in the container is occupied by the zeolite, which forms a horizontal surface at the top. In the upper part of the container there are devices for the liquid supply, and at the bottom there are outlet devices, through which the liquid may be discharged.

When starting the process, the container is filled with water that is particularly free from air, until it reaches just above the surface of the zeolite. The best way of carrying out the first filling process is to press the water slowly through the zeolite from below, thus eliminating the air from the interstices of the zeolite layer.

In order to avoid the formation of air bubbles while the process is in operation, all the liquids supplied to the container are first rendered free from air to the greatest possible extent, for instance, by placing them under vacuum. Air bubbles have the effect of lowering the efficiency of the plant. This is at least in part due to the fact that the bubbles obstruct the passage of liquid between the zeolite particles, thereby regarding the flow through the zeolite bed, causing disturbances in the uniform movement of the various layers of liquid (see later). Owing to the fact that vacuum sometimes occurs in certain parts of the zeolite bed, gas bubbles may be formed in the flowing liquid even if gas is present only in a dissolved condition in any one of the liquids which pass through the zeolite bed or beds. It is of great practical importance therefore that the liquids are free from gaseous constituents before they are subjected to the zeolite treatment. By means of suitable devices care is taken that the level of the liquid remains practically stationary through the entire process, that is to say, just above the surface of the zeolite. When the apparatus is in operation, the zeolite will thus remain in liquid all the time. For supplying the liquids while the process is in operation, a suitable spraying or distributing device is installed at the top of the container, having several outlets just above the surface of the layer of zeolite and evenly distributed above it, but under the level of the above mentioned liquid.

After the container has been filled with water, a calcium nitrate solution of a considerable degree of concentration is supplied through the aforementioned sprayers to the layer of sodium zeolite. The solution is evenly distributed over the surface of the zeolite and sinks downwards, displacing on its way a corresponding quantity of water, which runs away at the bottom of the container. During this process, the calcium from the nitrate solution gradually is incorporated in the zeolite, calcium zeolite being formed, whilst

sodium in equivalent proportions is forced out of the zeolite, sodium nitrate being formed in the solution. During the operation of the process an equally large quantity of liquid is discharged from the bottom of the container as that which is supplied to the zeolite at the top of the container.

At this stage in the process there is a nitrate solution on top and water just beneath it, and the liquids move gradually downwards through the zeolite. When a suitable period has elapsed, the supply of calcium nitrate solution is interrupted, water being supplied through the spray device instead. After a certain time there will thus be three different layers in direct contact with each other moving downwards through the zeolite, viz. first water, then the nitrate solution and finally water. As the nitrate solution now comes continually into contact with sodium zeolite that has not been converted, it will gradually become more enriched with sodium nitrate, whilst the quantity of calcium nitrate decreases. After fresh water has been supplied at the top of the container for a brief period, the water is turned off, and a sodium chloride solution is added, this having the effect of regenerating the used zeolite. When the regeneration is wanted to be as thorough as possible, a considerably larger quantity of this solution is used than of the nitrate solution. The difference in volume becomes still more marked, if a diluted sodium chloride solution is used, for instance sea water, which has been found to be suitable for this purpose in spite of the fact that it contains a plurality of different salts.

Under the assumption that a sufficiently high layer of base-exchanging substance is used, the following layers of liquid pass through the zeolite, counted from the top to the bottom: (1) chloride solution, (2) water, (3) nitrate solution, (4) water.

By degrees, as the layers move through the zeolite, the quantities of Ca in the chloride solution and of Na in the nitrate solution increase. After the water has been discharged from the bottom of the container, the nitrate solution flows down and is collected and evaporated, whereby the sodium nitrate is crystallized out. The mother liquor which chiefly contains calcium nitrate, and to which fresh quantities of calcium nitrate may possibly be added, is re-employed in the process.

The reason why a layer of pure water is inserted between the nitrate solution and the chloride solution is because this prevents the solutions from becoming intermingled. Consequently, the layer of water in principle ought to be so high that chloride and nitrate that diffuse into the water from each side do not reach the middle of the layer of water by the time it gets to the bottom of the container. In other words, there must still be some water left in the middle of the layer.

When collecting the nitrate solution, it will be possible to prevent any loss of nitrate by collecting at the same time half of the layer of water.

In order to prevent too great a dilution of the nitrate solution, such large quantities of water are not generally employed that complete separation of the nitrate solution and the chloride solution is obtained. The extent to which this is done largely depends upon how pure a quality of salt is required.

The chloride solution, which contains calcium chloride, obtained after the regeneration of the

zeolite, is also collected separately and may be evaporated, whereby calcium chloride and sodium chloride are obtained, the latter being reemployed in the process.

If sea water is used for regeneration purposes, the resulting calcium chloride solution becomes so diluted that it is sometimes considered worthless and is allowed to run to waste.

When the sodium chloride solution has been supplied to the zeolite at the top of the container for such a long time that the latter has become regenerated, clean water is again turned on, thereupon the nitrate of lime solution, then water, and then again the sodium chloride solution etc. as described above.

In this manner it is possible, by means of the zeolite and a sodium chloride solution, for instance sea water, to convert nitrate of lime into sodium nitrate in a continuous process.

#### Example

A cylindrically shaped container of an internal diameter of 1,5 metres is filled with zeolite (of a particle size between 0,4 and 0,8 mm) placed on a perforated plate. The height of the layer of zeolite is 6,4 m., and the gross volume thereof is 11,3 cubic metres. When the container is filled with liquid, which just reaches above the zeolite, the volume of the liquid is 80 per cent of the gross volume of the zeolite, or—in other words—it is 9,05 cubic metres.

At the commencement of the operation the zeolite consists of sodium zeolite, and the container is filled with water so that it covers the zeolite.

First, 2,11 cubic metres of calcium nitrate solution containing 52 gr. of  $\text{Ca}(\text{NO}_3)_2$  per 100 cubic cm., that is 1100 kilos of  $\text{Ca}(\text{NO}_3)_2$  in all, is supplied at the top of the container, and while this is in progress, 2,11 cubic metres of water is discharged from the bottom of the container.

Immediately the supply of nitrate solution ceases, 1,45 cubic metres of water is supplied at the top of the container, and directly after that, 4,75 cubic metres of sodium chloride solution containing 26 gr. of NaCl per 100 cubic metres, that is 1230 kilos of NaCl in all. Immediately after that, 1,6 cubic metres of water is supplied, then again 2,11 cubic metres of calcium nitrate solution. All the liquids supplied at the top of the container pass through the zeolite at a speed of 5 metres per hour. While passing through the zeolite, salt from the solution diffuses into the layers of water. In the present instance, the volume of water which was in the container at the commencement of the operation was 9,05 cubic metres. Had there been no diffusion, 9,05 cubic metres would have been discharged from the bottom of the container before the first nitrate ions could have been detected in the outlet, and the whole of the nitrate solution would have been contained in the same volume as before, i. e. 2,11 cubic metres, which could easily have been collected separately in the form of a nitrate solution.

Instead of allowing 9,05 cubic metres of water to flow away before collecting the nitrate solution, the collection thereof is begun—on account of the diffusion—as soon as 8,325 cubic metres has flown away, that is to say 0,725 cubic metres of the liquid is taken out prior to the original volume of the nitrate solution. Likewise, 0,725 cubic metre is removed after the original volume. In other words, 0,725 cubic m.+2,11 cubic m.+0,725 cubic m. is collected, this equalling 3,56 cubic m. in the form of a finished nitrate solution.

The attached diagram shows diagrammatically the conditions prevailing in the container at the moment the collection of the nitrate solution commences.

The collected nitrate solution (3,56 cubic m.) contains 728 kilos of  $\text{NaNO}_3$ , 312 kilos of  $\text{Ca}(\text{NO}_3)_2$  and 7 kilos of NaCl. Thus, about 70 per cent of the quantity of nitrate present in the solution is composed of sodium nitrate. About 5 per cent of the nitrate ions supplied are lost on account of the diffusion.

When evaporating the nitrate solution, about 90 per cent of the sodium nitrate present is obtained by crystallization. The mother liquid is then re-employed in the process as a nitrate charge.

Directly the nitrate solution has been collected 0,725 cubic m.+4,75 cubic m.+0,725 cubic m. equaling 6,2 cubic m. is collected in the form of a chloride solution. From the latter, calcium chloride can be produced. The sodium chloride thereby obtained is re-employed in the process for regenerating of the zeolite.

The quantity of water supplied at the top of the container after the sodium chloride solution may easily be greater than 1,6 cubic m. This is especially advantageous when desiring to produce nitrate that is as free as possible from chloride, because the greater the quantity of water used, the more effective is the washing out of the chloride from the zeolite.

When large quantities of water are supplied between the solutions, the middle part of the volume of water that is free from salt may be allowed to run to waste, the first and last parts being collected together with the adjoining solutions; by this means it is possible to avoid unnecessary dilution of the solutions.

Instead of only one container, it is also possible to use two containers or more. This is particularly advantageous when the sodium chloride solution used consists of sea water. In this case, very large quantities of sea water are needed for the regeneration process. The process can then be carried out advantageously in the following manner:

The regeneration is effected in one or more containers at a time by conducting sea water through the container or containers at a speed that is several times as high as that at which the calcium nitrate solutions or layers of water respectively pass through other containers, in which the conversion of the  $\text{Ca}(\text{NO}_3)_2$  into 2  $\text{NaNO}_3$  simultaneously takes place.

When using several containers, higher degrees of concentration of the nitrate are attained, provided only the middle, most highly concentrated part of the solution obtained from the container is collected, the less concentrated parts—coming before and after the middle part—being used as admixture in the other containers before and after a fresh supply of nitrate solution. By this means, it is possible to avoid any loss of nitrate.

When several containers are employed, the degree of conversion can be heightened by the following method:

The portion of nitrate solution supplied to a container is made say three times as large as that which is suitable, when only one container is employed. Only the first, more thoroughly converted part of the solution is collected as a finished solution after conversion has taken place in the container, whereupon the remainder or a suitable part thereof is conducted to another container containing newly regenerated zeolite.

To this container a concentrated calcium nitrate solution that has not been converted is then immediately supplied.

This can be repeated several times so that from container No. 2 only the first, more thoroughly converted, part of the solution is collected, the remainder or a suitable part thereof being transferred to container No. 3, containing newly regenerated zeolite etc. The degree of conversion will thus rise as nearly as possible to the state of equilibrium.

By combining the two mentioned methods, it is possible for the collected finished nitrate solutions to attain the highest possible degree of concentration and the highest possible degree of conversion.

When sea water is used as a regenerating solution the reuse of withdrawn solutions in the container will result in enriching the magnesium salts in the solutions passing through the containers and withdrawn thereupon.

Contrary to previously known methods, it is not the chief aim of the present process to attain complete conversion by means of the exchange of bases. It has, in fact, been found to be perfectly sufficient for an economic effectuation of the process, if conversion of 60 per cent is acquired.

The zeolite is not absolutely insoluble under the conditions described above. A part of it, therefore, becomes lost during the operation of the process. The solubility and consequently the loss is dependent upon the salt content in those liquids which pass through the zeolite, and it is therefore the clean water that dissolves the greater part.

It further appears that the silicic acid in the zeolite is more easily dissolved than the aluminium oxide, and this applies both when the zeolite is immersed in water and when it is contacted with salt solutions.

I have ascertained that the loss of zeolite can be reduced practically to nil, if a small quantity of a soluble silicate, for instance sodium silicate, is admixed to the water used in the process. Silicate can also be admixed to the solutions used, provided they do not already contain a sufficient quantity of silicic acid. It is especially advantageous to admix silicate to the sea water used for the regeneration of the zeolite in the production of sodium nitrate and to the freshwater employed between the salt solutions (nitrate and chloride solutions). Usually no silicate need to be added to calcium nitrate solutions of the character and origin above specified.

I have found it sufficient, in order to reduce the loss of zeolite to a minimum, to admix such a quantity of silicate that the water, and preferably the solutions too, contains 5-20 mgr. of  $\text{SiO}_2$  per litre. A suitable amount of  $\text{SiO}_2$  may for example be about 5 mg (total) to the litre of sea water and for example about 15-20 mg of  $\text{SiO}_2$  (total) to the litre of freshwater.

As it will be understood, the process described above can be used for a wide range of different salts, provided the salts cannot react with each other, unless base-exchanging substances are used. In the example described above, sodium chloride and calcium nitrate are used, which do not generally, that is to say, without the application of base-exchanging substances, react with each other to form sodium nitrate or calcium chloride with such a yield that that the process is practicable from a technical point of view.

As already mentioned the process according to the invention may be used with advantage as an intermediate step in the manufacture of alkaline metal nitrates from dilute nitrous gases. When this is done, one may proceed as follows:

Nitrous gases obtained by the catalytic oxidation of ammonia are passed through large percolation containers, wherein the nitrogen oxides are absorbed in water to obtain nitric acid.

The residual gases are treated with a soda solution, whereby a solution of sodium nitrate results.

The sodium nitrate solution is then passed through a layer of ammonium zeolite, whereby sodium zeolite and ammonium nitrate result.

The sodium zeolite is regenerated to ammonium zeolite by being contacted with ammonium carbonate solution. The sodium carbonate solution obtained by the zeolite treatment is thereupon employed to absorb further quantities of dilute nitrous gases.

The ammonium nitrate solution is reacted upon with lime or limestone to obtain nitrate of lime which is then treated in a zeolite container in the same manner as described in the above example, using a sodium chloride solution (f. inst. sea water) as a regeneration liquid for the zeolite. Sodium nitrate may be recovered from the solution in a solid form by evaporation and crystallization.

The same process may be used to produce potassium nitrate instead of sodium nitrate. In this case a solution of a potassium salt is used as a regeneration liquid for the zeolite.

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