

Potassium Nitrate Production Using a Molten Salt Technique

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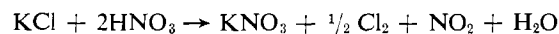
Production of potassium nitrate from potassium chloride was studied in a tubular molten salt reactor at atmospheric pressure and at temperatures of 150° to 385° C. Mixtures of potassium, sodium, and lithium salts were used to lower the melting point. Nitric acid (30 to 98 wt. %) was bubbled through the molten nitrate and chloride salt mixture containing 7 mole % chloride ion. Exit gases were absorbed; the resulting solution was analyzed analytically. Conversion of nitric acid to nitrate salt ranged from 23 to 61%. Higher conversion of nitric acid to nitrate salt resulted at lower tempera-

ture and higher nitric acid concentrations. Increases in the flow of nitric acid tended to decrease conversion. The exit gases contained primarily NO₂, Cl₂, HCl, and NOCl. The yield of elemental chlorine was found to be dependent upon reaction temperature and the conversion of nitric acid to nitrate salts. Yields as high as 90% are probable. In addition, solubility data for nitric acid and water in the molten salt are presented. A flowsheet and material balance of a proposed process also are described briefly.

Potassium nitrate is potentially a very valuable fertilizer if the price of it can be reduced sufficiently. It would be used as a replacement for potassium chloride which is presently used as the source of potash in most commercial fertilizers. Potassium chloride has the disadvantage that the chlorine (present as a chloride ion) has no agronomical value and may even be detrimental. Yet the chlorine accounts for almost 50% of its weight.

Interest in the production of potassium nitrate from potassium chloride is obvious based on several fairly recent patents (Beekhuis, 1962; Chadwick, 1962; Lovell and Lewis, 1959; Montecatini Societa Generale per l'Industria Mineraria e Chimica, 1962; Smith and Jacobs, 1960; Stengel, 1950; VEB Farbenfabrik Wolfen, 1961). For the last few years, Southwest Potash Corp. has been producing potassium nitrate and chlorine using potassium chloride and nitric acid as reactants (*Chem. Week*, 1965; Spealman, 1965).

Haug and Albright (1965) have recently publicized a new method for producing potassium nitrate and chlorine using a molten salt technique. The main reaction for many of their runs is represented as follows:



This reaction differs from the reaction in an aqueous medium in that hydrogen chloride and nitrosyl chloride are not formed. The runs were made at sufficiently high temperatures to maintain salt melts, and temperatures of about 310° C. or higher were required when potassium nitrate was produced. Although potassium nitrate melts at about 335° C., mixtures of it with potassium chloride and/or water at atmospheric pressure have reduced melting points. Temperatures as low as 250° C. were investigated

for mixtures of potassium and sodium salts which were used to make mixtures of potassium and sodium nitrates. In general, the reactions were quite similar for either potassium or sodium salts in the melt.

The results of Haug and Albright (1965) indicate that with pressures of perhaps 100 to 300 p.s.i.g., sufficient water (or steam) could be dissolved in melts containing primarily potassium nitrate to reduce the melting point by perhaps 100° to 200° C. Hence, potassium nitrate could be produced using this molten salt technique at temperatures from about 200° to 300° C. if the system was pressurized.

Additional information is needed so that the process can be better evaluated. In the present investigation, mixtures of potassium, sodium, and lithium salts were used so that melts could be studied from about 150° to 385° C. Data were obtained regarding the yields of products plus factors that affect the reaction at the different temperatures. A simplified flowsheet for a commercial process is proposed.

EXPERIMENTAL

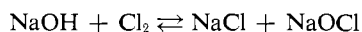
The reactor used was similar to the tubular reactor employed by Haug and Albright (1965). The one used in this investigation was constructed with a stainless steel tube that was 2³/₄-inch I.D. and 14 inches high. The bottom of the tube was closed with a stainless steel disk welded in place. Two openings were provided in the bottom, one for draining the melt, and the second as the opening for the line sometimes connected to the sparger for introducing the nitric acid. The top of the reactor was fitted with a gasket, and a reactor lid was bolted in place. Three openings were provided in the lid. One opening was used for a line that was sometimes connected to the sparger. This sparger was built of stainless steel, and 16 small openings were provided in it to produce small bubbles as the nitric acid vapors bubbled upward through the melt. Other openings in the lid were for the exit gas stream from the reactor and for the thermocouple well immersed in the salt melt.

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Exit gases from the reactor were bubbled through at least two glass absorber bottles. Various absorbents were used, but generally a 95% sulfuric acid solution was used in the first absorber and a 10% sodium hydroxide solution in the second. Nitrogen dioxide and water were absorbed in the first absorber. Nitrosyl chloride was also absorbed, and, in this medium, it reacted to form chlorine and nitrosyl sulfuric acid. Hydrogen chloride and chlorine were absorbed in the caustic solution. Chlorine reacted with the caustic as follows:



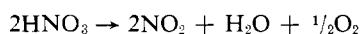
Total chlorine in the absorber solutions was determined by treating aliquot portions of the caustic solutions with 30% hydrogen peroxide in order to convert the hypochlorite ions to chloride ions. The Mohr technique (Kolthoff and Sandell, 1952) was then used to determine the total chloride content. A second aliquot sample of the caustic was acidified with sulfuric acid and boiled vigorously for 25 to 30 minutes in order to remove all free chlorine. The solution was then cooled, neutralized with sodium carbonate, and titrated using the Mohr technique to determine the residual chloride content of the solution. Preliminary tests with free chlorine and hydrogen chloride indicated that this technique was reliable for calculating total chlorine and the chloride content of the absorber solutions. The free chlorine content was determined by difference. No evidence was ever noted that nitric oxide was present in the exit gases from the reactor.

Provisions for adjusting the nitric acid flow rate to the reactor, for controlling the reactor temperature, and for collecting and analyzing the exit gases were similar to those of Haug and Albright (1965) except as noted.

RESULTS

Several runs made by Haug and Albright (1965) in a glass tubular reactor were repeated here also in a glass reactor. Good agreement of the results was noted in all cases. However, the glass reactor was found unsatisfactory for runs using mixtures containing lithium salts, since the lithium salts rapidly attacked and weakened the glass so that failure of the glass reactor resulted in most cases within a matter of hours.

Several preliminary runs were then made in the stainless steel reactor at the same conditions used by Haug and Albright (1965). In general, conversion of nitric acid to nitrate salts, which is defined as the number of chlorine atoms which have been displaced from the salt mixture for each molecule of nitric acid fed to the reactor, was about 10% lower on a relative basis in the stainless steel reactor than in the glass one. Probably the steel promotes somewhat greater decomposition of the nitric acid than glass:



Chloride salts are not very reactive with nitrogen dioxide.

In the previous investigation, Haug and Albright (1965) calculated conversions of nitric acid using the analytical results of the solutions obtained after the exit gases from the reactor had bubbled through the absorbers. Conversions were determined using the following equation:

$$\text{Conversion} = \frac{(\text{Cl})}{(\text{Cl}) + (\text{N})}$$

where Cl and N represent the total amount of chlorine and nitrogen found in the absorber solutions. Each was undoubtedly present primarily in some type of an ion. One of the basic assumptions of the above calculation is that one molecule of nitric acid is required to replace each atom of chlorine. Since only chloride or nitrate anions are found in the melt, this assumption is correct. An additional assumption of the above calculation, however, is that the value in the denominator equals the moles of nitric acid fed to the system. Earlier, this assumption was correct within experimental accuracy when melts at reasonably high temperatures were investigated. If, however, significant quantities of the nitric acid or chlorine-containing gases remain dissolved in the melts, the above method of calculating conversions would likely be quite inaccurate. The preliminary results of this investigation indicated that these compounds were being dissolved, especially in the melts at the lower temperatures.

Solubility Measurements. The saturated amounts of water (or steam) and of nitric acid that are dissolved in a melt containing 45 mole % lithium nitrate and the remainder potassium nitrate were determined by the procedure used earlier by Haug and Albright (1965). Figure 1 shows the results of these measurements made at atmospheric pressure using steam and 40 mole % (70 wt. %) nitric acid. Water solubility varied from 44 to 8.2 mole % from 150° to 250° C. Approximately three times as much water is dissolved as is predicted by Raoult's Law. Curves 2 and 3 indicate the solubilities of water and nitric acid in the melt which is saturated with 40 mole % nitric acid. This melt dissolves at temperatures above about 220° C., approximately 60% more water and about 50% more nitric acid than a melt containing 54.3 mole % sodium nitrate and the remainder potassium nitrate. Hence, the lithium nitrate promotes higher solubilities as compared with sodium nitrate. Reasonably smooth extrapolations of all three curves of Figure 1 can be made (as shown in Figure 1 for curves 2 and 3) to the boiling temperatures of the pure compounds at a pressure equal to the partial pressure involved.

Figure 1 clearly indicates that considerable amounts of both water and nitric acid will dissolve in the melt at

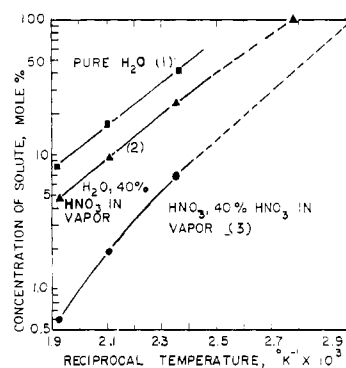


Figure 1. Solubility of H₂O and HNO₃

temperatures below 200° C. As a result, nitrogen was bubbled through the melts in order to strip chlorine or nitrogen-containing gases from them. The exit nitrogen stream from the reactor was bubbled through the absorber solutions to dissolve the product gases. The nitric acid conversions were then calculated by the procedure previously described.

The salt mixture containing 45 mole % (about 65 wt. %) lithium nitrate and the remainder potassium nitrate is essentially the eutectic mixture that melts at approximately 135° C. Phase information for this binary mixture was obtained in this investigation, and this information agrees quite closely to that published by Timmermans (1960).

Runs with Mixtures of Potassium and Lithium Salts. Approximately 1000 grams of a salt mixture containing 45 mole % lithium salts and the remainder of potassium salts was added to the reactor for each of 13 runs. The height of molten salt mixture, which was primarily nitrate salts, was about 6 inches in the reactor. The following variables were investigated:

- Temperatures: 155° to 307° C.
- Flow rates of nitric acid: 0.39 to 1.86 grams per minute
- Concentration of nitric acid: 30 to 98 weight %
- Chloride concentration in melt: about 7 mole % at start of run

The results of these runs as shown in Table I indicate the following factors:

Nitric acid conversions to nitrate salts increase significantly as the temperature is decreased. Conversions above 50% were obtained in several runs at about 155° C.

Conversions appear to decrease somewhat as the flow rate of nitric acid increases. (In other runs with a reactor with different dimensions, the reverse is found.)

When liquid nitric acid was added directly to the melts, the conversions were perhaps a little higher than when gaseous nitric acid was added.

More concentrated nitric acid gave somewhat higher conversions at 155° C.

Conversions with lithium-potassium salt mixtures at 300° to 350° C. were very similar to other runs of this

investigation and to runs by Haug and Albright (1965) in which sodium-potassium salt mixtures were used.

In Run 22, which was a 40-minute run, absorber solutions were collected and analyzed for each 10-minute period of the run. The moles of chloride found in each period were 0.000258, 0.0081, 0.0096, and 0.0154, respectively. The nitrogen purge was then started, and the moles of chloride recovered in the 40- to 50-minute period, the 50- to 170-minute period, the 170- to 380-minute period, and in the subsequent 16 hours were 0.0161, 0.0167, 0.0049, and a trace, respectively. The "apparent" conversion of nitric acid using the method previously outlined was calculated for each time period, and the results for the first 50 minutes are shown in Figure 2. The shape of the curve is similar to the one presented by Haug and Albright (1965) for a run using potassium salts at 352° C. In Run 22, more compounds were dissolved because of the lower temperature involved, and unsteady-state conditions obviously occurred during the entire run. Various degrees of unsteady-state conditions occurred undoubtedly in most, if not all, runs of the present investigation.

Production of Free Chlorine. Haug and Albright (1965) postulated that in many cases reactions of nitric acid with chloride salts results in yields of almost 100% elemental chlorine in addition to production of the nitrate salts. Production of HCl, NOCl, or NO₂Cl was considered to be of secondary importance. Two series of runs were made to determine the yields of chlorine, first for mixtures of potassium and sodium salts and second for potassium

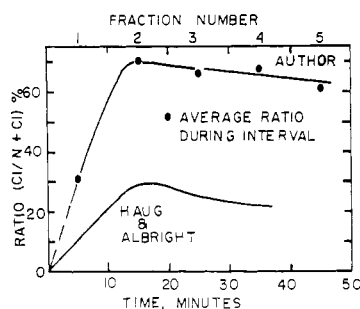


Figure 2. The ratio Cl/Cl + N vs. time

Table I. Runs with Mixtures of Potassium and Lithium Salts

Run No.	Initial Comp. of Melt, Mole % (Li, K) (NO ₃ , Cl)	Amount of Melt, G.	Reactant HNO ₃ , Wt. %	Melt Temp., °C.	Flow Rate HNO ₃ , G./Min.	Time, Min.	Conversion, %
8	6.87 Cl ⁻	1035	98	307	0.65	30	23
9	6.88 Cl ⁻	992	98	234	1.18	60	45
10	8.61 Cl ⁻	1044	98	206	0.89	30	49
11	6.84 Cl ⁻	1041	98	155	0.64	30	55
13	6.95 Cl ⁻	1088	98	155	0.53	30	61
14	6.76 Cl ⁻	1148	70	264	0.50	30	39
15	6.96 Cl ⁻	1124	70	206	0.55	30	49
16	6.87 Cl ⁻	1007	70	155	0.39	30	55
19	6.87 Cl ⁻	997	30	156	0.75	40	44
20	6.90 Cl ⁻	1037	30	155	0.84	30	44
21	7.11 Cl ⁻	997	30 (liquid)	156	0.70	30	52
22	7.00 Cl ⁻	1046	30 (liquid)	155	0.84	40	46
23	7.07 Cl ⁻	1021	30 (liquid)	155	1.86	25	49

salt melts. The yields increased for runs with a mixture of about 55 mole % sodium salts and the remainder potassium salts from about 70% at 350° C. to at least 80% in the range of 220° to 250° C. These particular runs were made in the steel reactor, and the conversions of nitric acid to nitrate salts were lower by at least 10% on an absolute basis than runs made by Haug and Albright (1965) in a glass reactor. In the steel reactor used, more nitric acid was apparently decomposed thermally. Runs were also made in the same steel reactor using potassium salt melts, and the fraction of potassium chloride converted to free chlorine varied from maximum values of 55% at 385° C. to 61% at 330° C. Hence, the amount of free chlorine produced may be somewhat less with potassium salts as compared to mixtures of potassium and sodium salts. Because the elemental chlorine content is determined by a difference technique, the elemental chlorine analysis may not be very accurate.

DISCUSSION

The molten salt technique has several important advantages as compared with other processes for the production of alkali metal nitrates such as potassium nitrate. The basic concept of the reactor is simple, the reactor is essentially instantaneous, and the alkali metal nitrates are produced in an essentially pure form so that recovery or purification steps are drastically reduced or simplified.

Production of elemental chlorine rather than other chlorine-containing gases is preferred commercially. Yields of elemental chlorine were found in this investigation for various salt mixtures to be dependent on both the reaction temperature and in addition on the conversion of nitric acid to nitrate salts. In general, higher conversions resulted in higher yields at least at temperatures above about 220° C. Improved conversions and yields as the temperature is lowered to 220° to 250° C. could also be expected for reactions involving pure potassium salts. (As was indicated earlier, pressurizing the system with steam results in a decreased melting point for potassium nitrate to 200° to 250° C. depending on the pressure used.) The following information supports this postulate:

Conversions of nitric acid and yields of chlorine agree reasonably well for various salt melts at temperatures from 335° to 385° C.

Trends noted at 335° to 385° C. also are similar within experimental accuracy.

Lantelme and Chemla (1963) have indicated that the mobilities of the potassium and sodium ions in melts differ. Some differences in the reactions might be expected as the relative concentrations of these ions are changed, but such differences would be expected to be rather small.

The yields of chlorine reported here are thought to be less than the maximum possible since nitric acid conversions were relatively low. Yields as high as 90 to 100% are probable if nitric acid conversions of essentially 50% were obtained. In this respect, a yield of 100% was actually reported by Haug and Albright (1965).

Removal of any HCl formed in the reaction should be quite easy. As Haug and Albright indicated, HCl reacts rapidly and essentially irreversibly when it is contacted with nitrate melts. Sufficient contact of the exit gases

with the nitrate melt would obviously remove any HCl present. This technique of HCl removal could serve as the first step in a new type of Deacon process. The chloride salt formed by HCl would in this case be subsequently reacted with nitric acid to form elemental chlorine and to reform the nitrate melt.

Small amounts of nitrosyl chloride, NOCl, and nitryl chloride, NO₂Cl, probably are produced in the process. Since commercial grade chloride salts, such as potassium chloride, sometimes contain small amounts of bromides, BrCl may also be produced in small quantities (Spealman, 1965). Southwest Potash Corp. removes these impurities in its process from chlorine and nitrogen dioxide by distillation.

Nitric acid conversions increased above 50% at temperatures less than about 200° C. At such conditions, the amounts of NOCl and NO₂Cl apparently increase at the expense of elemental chlorine. Possibly some HCl is produced at these temperatures because the reactions of HCl with the nitrate salt or of nitric acid with HCl to oxidize it are slow. Stengel (1950), for example, reported the production of significant amounts of HCl, even at relatively high temperatures.

The method of contacting the nitric acid with the melt is important. Care must be taken to minimize the thermal decomposition of the nitric acid before it is dissolved in the melt which, as determined by Haug and Albright (1965), is the location of the reaction. Variations in the flow rates, height of molten salt, type of sparger, degree of pre-heating the nitric acid, liquid or vapor state of the acid, and the concentration of the acid have all been shown to have some effect on the reaction. Probably all of these factors are important primarily because of their complex relationship to decomposition and solubility. The concentration of nitric acid used in a commercial process would depend primarily on the relative costs of acid and to a lesser extent on differences in the reaction.

PROPOSED PROCESS

The proposed process for producing alkali metal nitrates and chlorine is shown in Figure 3. The process will be described using potassium nitrate as the example. Basically, the process consists of four sections.

The first portion of the process is a solution tank in which potassium chloride is dissolved in the melt of potassium nitrate. The best procedure will probably be to add continuously finely ground KCl to the melt. Agitation and heat will be required to obtain a solution of perhaps 7 mole %, or even higher, KCl in the melt at the desired temperature.

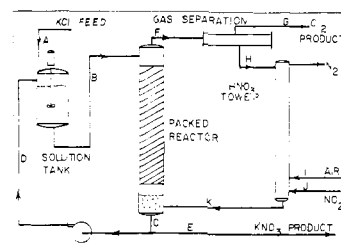


Figure 3. Flowsheet proposed process

Table II. Flows in Proposed Process

	(Basis: 1 hour)
Stream A	7.3 tons KCl
Stream B	139 tons total (7.3 tons KCl and 131.7 tons KNO ₃)
Stream C	142 tons KNO ₃
Stream D	132 tons KNO ₃
Stream E	10 tons KNO ₃
Stream F	14.7 tons total (6.9 tons water, 4.4 tons NO ₂ , 3.4 tons chlorine)
Stream G	3.4 tons chlorine
Stream H	12.05 tons total (7.6 tons water, 4.45 tons NO ₂)
Stream I	1.9 ton O ₂ plus 7.1 tons N ₂
Stream J	4.4 tons NO ₂
Stream K	17.3 tons total (12.1 tons HNO ₃ plus 5.2 tons water)

The molten mixture of KNO₃ and KCl then flows to the second portion of the process, which is the reactor. Several reactor arrangements are possible. One arrangement is to use a series of continuous-flow stirred-tank reactors in which the melt and nitric acid vapors flow counter-current to each other. Another suggested arrangement is to use a column reactor, such as a packed tower. In this case, the melt and vapors also flow countercurrent to each other. Ceramic packing and a ceramic innerliner should minimize corrosion problems plus nitric acid decomposition. When the reactor is operated at 200° to 250° C. and at several hundred p.s.i.g. or perhaps even less, nitric acid conversions up to almost 50% can be expected. Relatively little nitric acid will probably decompose at these conditions. Vaporization of the nitric acid can be accomplished using a heat exchanger, but corrosion problems would be severe. The suggested method of vaporization is to inject the liquid nitric acid directly into the exit melt. The net result of this technique is that the chloride content of the melt will be reduced to very low values, and the nitric acid will be vaporized without using heat transfer surfaces for vaporization. Some heat will have to be provided to the melt to maintain a sufficiently high temperature so that freezing does not occur prematurely. Information that should be useful in designing the reactor has been presented by Haug and Albright (1965).

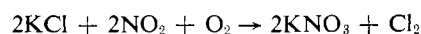
The molten KNO₃ from the reactor is divided into two streams. Most of the melt is recycled to the solution tank, and the remainder is the KNO₃ product. This product melt may need to be stripped with nitrogen or other inert gas to remove undesired dissolved material. For safety reasons, air probably should not be used. The molten KNO₃ could be prilled or allowed to solidify in other desired manners.

The exhaust gases from the reactor contain chlorine, water vapor (from the desired reaction of KCl with HNO₃, the entering nitric acid feed, and possible thermal decomposition of part of the nitric acid), nitrogen dioxide (from the desired reaction and nitric acid decomposition), oxygen (from thermal decomposition of nitric acid), plus some NOCl, NO₂Cl, and impurities such as BrCl. These latter gases must be separated to recover the chlorine

and nitrogen dioxide. A condensation and fractionation technique similar to that used by Southwest Potash Corp. (Spealman, 1965) should be quite effective for the third phase of the process. Combinations of partial condensations and/or selective absorption techniques might also be satisfactory. NOCl and NO₂Cl would probably be recycled since equilibrium concentrations of these compounds would eventually be formed.

In the last phase of the process, the recovered nitrogen dioxide plus make-up nitrogen dioxide (obtained by the oxidation of ammonia) are used to produce nitric acid in a conventional manner. The nitric acid so formed is used as feed to the reactor.

Table II indicates the predicted flow for a unit making 84,000 tons of KNO₃ and 28,500 tons of chlorine per year. The basic over-all process is essentially represented by the following stoichiometric equation:

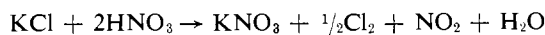


In making the calculations for Table II, the following assumptions were made:

The KNO₃ product contains 1.0 wt. % KCl and the remainder is KNO₃. Even higher purities could be obtained in this process if desired.

Seventy weight per cent nitric acid was used.

Nitric acid reacts as follows in the reactor:



If some nitric acid decomposes, more nitrogen dioxide and water will be produced and, in addition, oxygen. Calculations indicate that even if rather significant amounts of nitric acid decompose, the amounts of oxygen in the exit gas stream from reactor are quite low.

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