Preparation and characterisation of potassium ammonium nitrates \( \text{K}_x\text{(NH}_4\text{)}_{1-x}\text{NO}_3 \)

The use of ammonium nitrate as an ingredient in explosives has increased significantly around the world due to demand for minerals and raw materials. Ammonium nitrate is a feedstock for making emulsion explosives as well as ammonium nitrate and fuel oil explosives, both commonly applied in open-cut mining operations. Decomposition of ammonium nitrate may release red clouds of nitrogen oxides, especially under wet-rock blasting conditions. Doping \( \text{NH}_4\text{NO}_3 \) with potassium may decrease the amount of emitted \( \text{NO}_x \). In this contribution, we report the preparation and characterisation of co-recrystallised ammonium and potassium nitrates, for future investigations on emissions of \( \text{NO}_x \) from decomposition of these materials. The results indicate the existence of solid solutions of potassium and ammonium nitrates below 1 mol % K and between 5 and 25 mol % K.

1. INTRODUCTION

Ammonium nitrate (AN) constitutes a major component in industrial explosives, used mainly in formulating ammonium nitrate and fuel oil (ANFO) explosives, as well as emulsion explosives. Under adverse conditions of rock type and presence of ground water, blasting of ANFO, or blends of ANFO and emulsion explosives may release substantial amounts of nitrogen oxides, especially under lean fuel oil conditions (Sapko et al. 2002). In recent years in Australia, the emissions of \( \text{NO}_x \) during blasting in mining operations have come under intense scrutiny of regulatory bodies and concerned citizens, as such emissions pose environmental and health risks; in particular, when orange clouds, characteristic of high levels of \( \text{NO}_2 \) and \( \text{NO} \), do not dissipate rapidly and drift into populated areas surrounding the mines. Thus, there is a great interest in industry for gaining improved understanding of the formation of \( \text{NO}_x \) during blasting, and finding practical solutions to remedy the problem (Rowland et al. 2001; Sapko et al. 2002).

Decomposition chemistry of ammonium nitrate has been studied extensively and several modes of decomposition reaction mechanisms have been proposed, as function of pressure, temperature, confinement, heating rate, samples sizes, and presence of
alkali and alkali earth nitrates (Gunawana and Zhang 2009; Jones et al. 1999; Langfelderova 1982; Oxley et al. 1992; Turcotte et al. 2003). The initial step in decomposition of AN in the condensed phase involves an endothermic proton transfer from the ammonium ion (NH$_4^+$) to the nitrate ion (NO$_3^-$) to form nitric acid (HNO$_3$) and ammonia (NH$_3$), followed by decomposition of nitric acid itself (Eq. 1) (Brill et al. 1993; Brower et al. 1989; Chien et al. 2010; Oxley et al. 1989; Sinditskii et al. 2005; Vyazovkin et al. 2001; Wu et al. 2007). Although, several reaction pathways for the proton transfer have been proposed by different research groups, consensus exists that the overall decomposition process of AN yields mostly H$_2$O and N$_2$O (Eq. 2), (Brill et al. 1993; Brower et al. 1989; Chien et al. 2010; Oxley et al. 1989; Sinditskii et al. 2005; Vyazovkin et al. 2001; Wu et al. 2007).

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3(g) + \text{HNO}_3(g) \quad (1)
\]

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \quad (2)
\]

It is also well appreciated that fast decomposition of ammonium nitrate between 200 to 230 °C results in release of NO gas (Eq. 3) (Oommen and Jain 1999).

\[
2\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{NO} + 4\text{H}_2\text{O} \quad (3)
\]

Oommen and Jain (1999) reported that AN deflagration engenders a different reaction mechanism that yields both NO and N$_2$O (Eq. 4), while AN detonation follows yet another reaction pathway (Eq. 5) that produces N$_2$ and NO$_2$. The presence of NO and NO$_2$ in decomposition gases of AN was also observed by other researchers (Brill et al. 1993).

\[
8\text{NH}_4\text{NO}_3 \rightarrow 5\text{N}_2 + 4\text{NO} + 2\text{NO}_2 + 16\text{H}_2\text{O} \quad (4)
\]

\[
4\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 2\text{NO}_2 + 8\text{H}_2\text{O} \quad (5)
\]

In mining, the formation of nitrogen oxides (mainly N$_2$O, NO, and NO$_2$) during thermal decomposition, deflagration or detonation of ammonium nitrate poses risks to both people and the environment. It has been reported that addition of alkali and alkali earth salts to AN can lower the emissions of nitrogen oxides during AN decomposition (Kaljuvee et al. 2009; Klimova et al. 2011; Oxley et al. 2002; Rudjak et al. 2010; Sapko et al. 2002).

Oxley et al. (Oxley et al. 2002) observed that thermal stability of AN doped with alkali and alkali earth nitrates is related to the N$_2$O/N$_2$ ratio in gaseous products. These authors ground different weight percentages of calcium, potassium, and sodium nitrate salts together with AN, and studied the thermal decomposition of the mixtures. The results indicated that the more stabilising the additives, the lower the N$_2$O/N$_2$ ratio. Unfortunately, Oxley et al. reported no measurements of concentrations of NO and NO$_2$. Two further observations of Oxley et al. are important. Firstly, when calcium, potassium, and sodium nitrates were added to AN, there was almost no
change in the decomposition temperatures of the mixtures compared with the decomposition of pure AN. Secondly, a mixture containing 10 mol % potassium nitrate exhibited a lower N₂O/N₂ ratio compared with that of pure AN. Likewise, other researchers have demonstrated increased stability of AN doped with K as a consequence of the transformation of AN from crystalline phase IV to crystalline phase III (Li et al. 2009; Oommen and Jain 1999; Vargeese et al. 2010; Wu et al. 2008). However, the mode of decomposition of mixed nitrate crystals of AN doped with K remains unknown, prompting the present study.

In this contribution, we investigate the effect of the presence of potassium nitrate on the crystal structure of mixed salts for potential application in industrial explosives, to minimise the formation of nitrogen oxides. In the first phase of the study, reported in this contribution, we attempt to crystallise solid solutions of potassium and ammonium nitrates, and characterise them by powder XRD (X-ray diffraction), SEM-EDS (scanning electron microscopy – energy dispersive spectroscopy) and ICP-OES (inductively coupled plasma – optical emission spectroscopy). We also report the formation of two crystalline phases at low (2-4 mol %) and high (>20 mol %) concentrations of potassium in the crystallisation solution; mol % is based only on K⁺ and NH₄⁺ and does not include the solution water. The thermal and explosive decomposition of the mixed salts will be reported in a subsequent publication.

2. EXPERIMENTAL

2.1. Materials

Pure ammonium nitrate and potassium nitrate salts were used as precursors in the preparation of mixed salts. AN (crystalline 99.9 wt % pure (dry basis)) was supplied by Dyno Nobel Asia Pacific Pty Ltd. Potassium nitrate salt (UNIVAR reagent 99.5 %) was purchased from Ajax Chemicals.

2.2. Crystallisation

A total of 4.0 g of AN and KNO₃ salts were dissolved in 1 mL of de-ionised water to form a supersaturated solution. The concentration of KNO₃ in the mixture was varied from 1 to 25 mol %. The supersaturated solution was placed in hot water bath at 80 °C while the solution was agitated every 15 min intermittently for complete dissolution. After heating the solutions for 1 h at 80 °C, the solutions were quenched in ice-cold water bath at 1 °C to effect nucleation, growth, and precipitation of mixed nitrate salts. Precipitated salts were filtered immediately. All precipitated samples were stored in a desiccator for at least 48 h before characterisation.
2.3. **Structural analysis**

Structural characterisation of NH₄NO₃, KNO₃, and NH₄NO₃/KNO₃ mixtures were analysed by Philips X’pert-MPD X-ray Diffraction system using Cu Kα₁. XRD characterisations of samples were conducted under conditions of room temperature and atmospheric pressure. Samples were scanned from 10 ° to 70 ° for a total duration of 20 min with a step size of 0.008 ° at 40 kV and 40 mA operating power.

2.4. **Morphological analysis**

Recrystallised nitrate salts were imaged using Philips XL30 SEM coupled with Oxford ISIS EDS for elemental analyses. Nitrate salts were carbon coated using SPI Carbon Coating Unit prior to imaging. SEM images and EDS spectra of the nitrate salts were obtained by scanning samples at 15 kV.

2.5. **ICP analysis**

The concentration of metal cations in potassium nitrate and mixed nitrate salts were quantified using Varian 715-ES ICP Optical Emission Spectrometer. Amounts of 250 mg of nitrate salts were dissolved in 500 ml of de-ionised water. Sample solutions were transferred via Varian SPS 3 sample preparation system for analyses in ICP-OES. High-Purity Standards ICP multi element standard solution containing eight metal cations in 2.0 % HNO₃ was used for calibration.

3. **RESULTS AND DISCUSSION**

X-ray powder diffraction (XRD) pattern of recrystallised AN is shown in Fig. 1. At 2θ of 28.9 °, the 100 % peak, which corresponds to (111) surface and d-spacing 3.085 Å, matched very well with crystalline AN phase IV as can be seen in Fig. 1. It was also observed that all other peaks characteristic of AN phase IV also matched with those displayed by this sample. AN phase IV has orthorhombic structure that is stable between -18 and 55 °C when dry or between -18 and 32 °C in the presence of moisture (Dellien 1981; Oommen and Jain 1999).

Addition of 1 mol % KNO₃ to AN during co-recrystallisation shows no visible modification of the XRD pattern compared with pure AN phase IV. This amount of KNO₃ is probably at the detection limit of the XRD analysis. However, it stands to reason to suggest that the crystal lattice of AN could accommodate 1 mol % content of K⁺ ions as the ionic radius of K⁺ (0.133 nm) is only slightly smaller than that NH₄⁺ (0.143 nm). Hence, NH₄⁺ could undergo substitution by minor amount of K⁺ in the crystal structure without much distortion. Usually small inclusions in pure phase cause peak broadening in XRD pattern of the main component due to stress in the crystal structure which is observed as a small shift in the d-spacing. This is because a number of parallel planes of small inclusions may prevent diffraction to occur at
precise angles. However, there was no visible shift of the XRD peaks of this sample compared with pure AN phase IV. Further analysis of a co-recrystallised sample containing 1 mol % KNO₃ and 99 mol % AN by EDS indicated the presence of K in
the sample. In addition, ICP-OES measurements of this sample confirmed the presence of K. This led us to a conclusion that co-recrystallisation of 1 mol % KNO₃ and 99 mol % AN probably resulted in a complete solid solution of potassium ammonium nitrate without much distortion of the AN phase IV crystal structure.

Figure 3 shows an XRD spectrum of a co-recrystallised sample containing 2 mol % KNO₃ in balance of AN. The spectrum illustrates two crystalline phases of AN; that is, AN phase IV with a small trace of AN phase III. AN phase III has an orthorhombic structure which is stable between 32–84 °C but is less dense, by about 3.84 %, than AN phase IV (Oommen and Jain 1999). Co-recrystallisation of 2 mol % KNO₃ and 98 mol % AN commences to change the crystal structure of AN from phase IV to III in order to accommodate the increased modal concentration of K⁺ ions. This is evident in the XRD pattern at 2θ of 22.7 ° (60 % peak), and 27.7 ° (100 % peak) which correspond to (111) and (021) planes of AN phase III as shown magnified in the inset to Fig. 3.

Figure 3. XRD patterns of co-recrystallised AN containing 2 mol % KNO₃ showing phase III (red) and phase IV (blue).

In Fig. 4, the XRD spectrum of recrystallised samples confirms that increasing KNO₃ concentration to 3 mol % in balance of AN elevates the content of phase III in the multi-phase AN. When modal composition of KNO₃ increases to 5 mol %, the XRD peak at 2θ of 27.7 ° matches well the (210) surface that corresponds to 100 % peak of K₀.₀₅(NH₄)₀.₉₅NO₃. K₀.₀₅(NH₄)₀.₉₅NO₃ displays orthorhombic structure similar to phase III of AN. Further increment in KNO₃ concentration from 5 to 20 mol %,
during preparation, reveals single phase $K_{x}(NH_{4})_{1-x}NO_{3}$ with no separate phase of potassium nitrate, according to the XRD results as presented in Fig. 5 and Table 1. From the overlaid spectra of Fig. 5, the largest peak at $2\theta$ of 34.2 ° corresponds to $d$-spacing of 2.617 Å in samples containing 10, 15 and 20 mol % K. However, crystals obtained from the solution of 25 mol % KNO$_3$ and 75 mol % AN reveal the presence of pure KNO$_3$ phase, as indicated by the peak at $2\theta$ of 26.9 ° in the XRD measurement. This demonstrates that 25 mol % substitution of NH$_4^+$ by K$^+$ exceeds the solid solubility limit of AN crystal structure, causing the precipitation of pure KNO$_3$, when co-recrystallised with AN.

![Figure 4. XRD patterns of co-recrystallised AN containing 3 mol % KNO$_3$ showing phase III (red) and phase IV (blue).](image)

Recrystallisation of pure AN from hot saturated solution by direct quenching in ice-cold water bath at 1 °C resulted in plate and needle-like shapes, consistently with the results of other researchers (Vargeese et al. 2009). SEM images could not be taken at magnification higher than 10,000×. The samples seemed to evaporate at higher magnification even if the voltage was set as low as 5 kV. The SEM images of recrystallised pure AN displayed sheet-like surfaces with a few embedded needle-like crystals, as shown in Fig. 6. However, the morphology of samples of AN containing KNO$_3$ exhibited fused crystals with numerous cracks along the crystals boundaries, as illustrated in Figs. 6-8. It appears that increasing concentration of K in solid solutions induces the formation of more distinct crystals with micro tree-like cracks in addition to crystal boundaries. This demonstrates the effect of rising stress on the crystal structure at increasing concentration of K, leading to separation of the material into two phases, once modal content of K reaches 25 mol %.
EDS analyses of single crystals of nitrate salts were not possible, but bulk qualitative EDS of recrystallised nitrate salts indicated the presence of potassium in all the potassium ammonium nitrate salts. Figures 9-11 illustrate the characteristic peaks K_α1 and K_β1 of potassium, which appear at 3.314 and 3.590 keV respectively. As expected, the intensities of the characteristics potassium peaks of K_α1 and K_β1 increase with increasing concentration of KNO_3 in the co-recrystallised salts.

Table 1. Summary of powder XRD results of co-recrystallisation of KNO_3 and AN salts.

<table>
<thead>
<tr>
<th>mol % KNO_3*</th>
<th>mol % KNO_3**</th>
<th>Phase(s) Present XRD</th>
<th>Comments</th>
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<tr>
<td>0.00</td>
<td>1.06 ± 0.01</td>
<td>AN phase IV</td>
<td>Single phase</td>
</tr>
<tr>
<td>1.00</td>
<td>1.91 ± 0.03</td>
<td>AN phase IV</td>
<td>Single phase</td>
</tr>
<tr>
<td>2.00</td>
<td>2.57 ± 0.01</td>
<td>AN phase III and IV</td>
<td>Multi-phase of AN</td>
</tr>
<tr>
<td>3.00</td>
<td>3.43 ± 0.03</td>
<td>AN phase III and IV</td>
<td>Multi-phase of AN</td>
</tr>
<tr>
<td>4.00</td>
<td>4.24 ± 0.05</td>
<td>AN phase III and IV</td>
<td>Multi-phase of AN</td>
</tr>
<tr>
<td>5.00</td>
<td>11.77 ± 0.09</td>
<td>K_0.05(NH_4)_0.95NO_3</td>
<td>Single phase</td>
</tr>
<tr>
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<td>17.06 ± 0.18</td>
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</tr>
<tr>
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<tr>
<td>25.00</td>
<td>97.57 ± 1.66</td>
<td>K_x(NH_4)_{1-x}NO_3 and KNO_3</td>
<td>Multi-phase of KNO_3 and AN</td>
</tr>
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</table>

* refers to mol % KNO_3 in AN in crystallising solution, on water free basis
** refers to mol % KNO_3 in mixed crystals as measured by ICP OES

Figure 5. XRD patterns of co-recrystallised AN containing 5-25 mol % KNO_3.
Figure 6. SEM images of pure AN (left), and 1 mol % KNO$_3$-AN (right).

Figure 7. SEM images of 2 mol% KNO$_3$ / AN (left), and 4 mol% KNO$_3$ / AN (right).

Figure 8. SEM images of 10 mol % KNO$_3$ / AN (left), and 25 mol % KNO$_3$ / AN (right).
Figure 9. EDS spectra of recrystallized pure AN (left), and 4 mol % KNO₃/AN (right).

Figure 10. EDS spectra of 4 mol % KNO₃/AN (left), and K₀.₀₅(NH₄)₀.₉₅NO₃ (right).

Figure 11. EDS spectra of K₀.₁₀(NH₄)₀.₉₀NO₃ (left), and K₀.₂₀(NH₄)₀.₈₀NO₃ (right).
4. CONCLUSION

Attempts were made to prepare mixed potassium ammonium nitrate salts for potential application to minimise the formation of NOx during detonation of AN explosives. Co-recrystallised mixed nitrate salts were prepared from pure ammonium and potassium nitrate precursors. Powder XRD, SEM-EDS, and ICP-OES were used to characterise the co-recrystallised salts. Co-recrystallisation of 1 mol % KNO3 and AN resulted in a single phase, identified as AN phase IV. Increasing the concentration of KNO3 to between 2 and 4 mol % resulted in the appearance of an additional AN phase. Loadings of 5 to 20 mol % KNO3 formed solid solution of the form Kx(NH4)1-xNO3, which has orthorhombic structure similar to pure AN phase III. Attempts to increase KNO3 content in AN to 25 % led to the formation of two phases, solid solution of the form Kx(NH4)1-xNO3 plus small phase precipitation of pure KNO3.

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References