The Potential Destructive Impact of Non-fuel Containing Nitrate Salts Jimmie C. Oxley University of Rhode Island February 2007

In rating chemicals of concern as potential explosive precursors, it cannot be assumed that any oxidizer mixed with a fuel creates an explosive. The US National Research Council (NRC) report of 1998¹ used a number of criteria to select the nine chemicals of most concern, but available quantities and a record of previous use weighed heavily. The Council of Australian Governments (COAG) Review of Hazardous Materials² developed an equation, which for explosive precursors, calculated the security risk as the product of impact x threat. Impact was a rating of the power and detonation velocity of the explosive made from the precursor. AN-based explosives typically have low detonation velocities in the range 2500 to 3500 m/s (cf. 6900, TNT or 9000 m/s, HMX). It would be expected that other nitrates would perform more poorly than AN. Although they are occasionally mixed into various explosive mixtures in small quantities, there are no reports of XNO₃/fuel oil explosives. To the contrary, testing at about the 250 pound scale (12" x 60") (about 30 cm by 152 cm) proposed in NRC report, has shown X = Ca, K, or Na, no detonation occurs, even using a 5 pound Pentolitethat when booster. Under identical conditions, ANFO detonated with a detonation velocity ~3400 m/s.³ The only common "explosive" made with the alkali and alkaline earth nitrates is black powder. It is not a high explosive at all, but a propellant (otherwise it would not be used as gun powder). Its burn rate does not exceed 500 m/s.4

One of the reasons formulations using the alkali and alkaline earth nitrates, instead of AN, are likely to be propellants rather than explosives is that a great portion of their weight is made up of atoms which are not easily converted to gas—Ca, K, or Na. Thus, some of the oxygen of the formulation is diverted to the formation of products other than the working fluid (CO₂, N₂, H₂O) formed by high explosives.

 $25 \text{ NH}_4\text{NO}_3 + \text{C}_8\text{H}_{18} \rightarrow 8 \text{ CO}_2 (g) + 59 \text{ H}_2\text{O} (g) + 25 \text{ N}_2 (g)$

 $10 \text{ KNO}_3 + \text{C}_8\text{H}_{18} \rightarrow 3 \text{ CO}_2 (g) + 9 \text{ H}_2\text{O} (g) + 5 \text{ N}_2 (g) + 5 \text{ K}_2\text{CO}_3 (s)$

where (g) stands for gases and (s) for solids.

Therefore, without testing to the contrary, the destructive *impact* of the nitrate salts, calcium (CN), potassium (KN), and sodium (SN), should be considered low.

The COAG *threat* was based on two parameters: feasibility and intelligence. Feasibility took into account five factors. Three of these should be identical for all three nitrate salts (CN, KN, SN): <u>utility</u>, an estimation of the ease with which the chemical in question can be converted into an improvised explosive; <u>capacity to scale-up</u> to large devices; <u>detectability</u> of the chemical. The last two factors, availability and ease of acquisition, relate to the amount of material for sale and the ease with which a terrorist could acquire it. In Australia the availability of KN is somewhat less than that of CN (30,000 ton CN and 13,000 ton KN are sold annually). Both CN and KN fertilizers are primarily used in the same sectors (vegetables and fruits); thus, they have identical ease

of acquisition. SN is used in lower amounts in Australia (about 3,000 ton annually); it is mainly used in the industrial sector (natural SN is approved in organic agriculture in the United States but not in Australia). To my knowledge none of these three nitrates has been the main material for large-scale bomb making.

At the 250 pound scale, in the standard test protocol suggested by the NRC to identify detonable materials, there is no evidence that any of the single nitrate salts [Ca(NO₃)₂, KNO₃, or NaNO₃] were detonable with added fuel oil.³ Other fertilizers containing AN such as CAN (calcium ammonium nitrate with 27% N) detonated with a detonation velocity ~2500 m/s under the same test conditions even with smaller boosters, showing at least that the test is effective to its purpose.⁵ It is possible that the single nitrate salts might be made to detonate on an extremely large scale or with an energetic fuel; however, to date no such test protocols have been designed or recommended. The U.S. Bureau of Alcohol Tobacco, Firearms and Explosives (ATF) has grouped all the alkali and alkaline earth nitrates as equal risk.⁶ Indeed, the U.S. NRC report grouped CN and SN together and discussed KN separately, but all were rated as having "low" overall potential for use (see Table).¹ What is surprising is that all three nitrates- calcium nitrate (CN), potassium nitrate (KN) and sodium nitrate (SN) have not been treated equally by COAG.² Perhaps this oversight has its roots in the late historical development of CN, as explained below.

Like all the nitrate salts considered herein, calcium nitrate, also called Norgessalpeter (Norwegian saltpeter), is a white water-soluble salt. With four waters of hydration, [Ca(NO₃)₂.4H₂O], CN contains 11.9% nitrogen by weight. CN was first produced in the early 1900's. To compete with Chilean saltpeter (sodium nitrate) fertilizer which contains between 15 and 16% nitrogen, AN was added to CN at the 5% level and the water of crystallization was decreased from four to two H₂O. Thus, the nitrogen content increased to 15.5%. (The formula of the double salt is 5Ca (NO₃)₂.NH₄NO₃.10H₂O). This calcium nitrate fertilizer was classified in Europe as an AN-containing fertilizer, but it had such low content of AN that it was exempted from the AN fertilizer safety regulations.⁷Calcium nitrate tetra-hydrate (CN), the original calcium nitrate, was classed as any other single nitrate salt with a cation from the alkali metal (lithium, sodium, potassium, rubidium and cesium) or alkaline earth metal (magnesium, calcium, strontium and barium) families.

More than 25 years ago, when use of nitrogen-containing fertilizer in terrorist bombs was not yet envisioned, nitrate fertilizers were only a **safety** and not a **security** concern. AN and those three single industrial nitrate salts (CN, SN, KN) were all classified in the 5.1 oxidizer hazard class and regulated accordingly. CN fertilizer was not because tests were done to show that, in its commercial form, it was a weaker oxidizer than the standard test reference. Similar arguments and logic could be applied to KN and SN in their prilled form.⁸ Later, when nitrate fertilizers became a security concern (mostly because of the widespread terrorist use of ANFO), the focus was first drawn on those that already were regulated on safety grounds as class 5.1 oxidizers (even though none of them were, and still are not, classified as explosives).

The irony of this chain of events is that calcium nitrate tetra-hydrate $(Ca(NO3)_2.4H_2O)$ which is classified in the 5.1 hazard class $(UN1454)^9$ is, in fact, a weaker explosive precursor than the CN fertilizer which contains AN and half as much water. This conflicting regulation remains unaltered today. SN and KN remain classified as oxidizers, until their new test data can be reviewed,⁸ as it has been for magnesium

nitrate.¹⁰ Therefore, in some countries, due to the confusion of safety versus security criteria, SN and KN are wrongly singled out for regulation. Indeed, only CN fertilizer is in the appropriate class from both a safety and security standpoint.

It is my conclusion that with the information available for CN, KN, and SN salts they should be all regulated in the same fashion.

Footnotes and References:

1. "Containing the Threat from Illegal Bombings: An Integrated National Strategy for Marking, Tagging, Rendering Inert, and Licensing Explosives and Their Precursors;" National Academy Press; 1998.

2. "A Discussion Paper on the Control of Chemicals of Security Concern;" Council of Australian Governments Review of Hazardous Materials; Nov. 30, 2006.

3. "Evaluation of Propagation of Detonation Ammonium Nitrate, Sodium Nitrate, Calcium Nitrate, and Potassium Nitrate Mixed with Diesel Fuel" EMRTC report #FR04-46; T. Zimmerly; C. Hockensmith; Mar. 2005.

4. Although black powder is not a high explosive, the US Department of Transportation, and the UN classify it as a "Class A High Explosive" hazard class for shipment i.e. for **safety** reasons because it is so easily ignited and not for **security** reasons. Indeed, all strong oxidants are by nature unstable (safety risk), but the level of instability is **not** a measure of its strength as an explosive (security risk). The hazard class has to do with the level of risk that the substance would decompose burn, deflagrate or detonate involuntarily during manufacture, transport or storage. It is a measure of *sensitivity* and *stability*, but it is not a measure of the explosive *strength*. It seems unlikely that terrorists would go through the trouble of using KN or SN as raw materials, blend the nitrate with sulphur and a special type of charcoal to end up with a hygroscopic, propellant with such low yield that it would require handling large quantities of this highly sensitive (from a safety point of view) material.

5. "Analysis of field measurements conducted at the field testing facilities of SQM, Antofagasta, Chile" Dyno Consultant Latin America; W. Adamson; Dic.2004.

6. In the 2002 List of Explosive Materials, ATF has added five terms to the list of explosives. One of the additions was "nitrate explosive mixtures." "*Nitrate explosive mixtures*' is intended to be an all-encompassing term, including all forms of sodium, potassium, barium, calcium, and strontium nitrate explosive mixtures." http://www.globalsecurity.org/military/systems/munitions/explosives-list.htm

7. Under the rule: "The commercial grade of calcium nitrate fertilizer, when consisting mainly of a double salt (calcium nitrate and ammonium nitrate) containing not more than 10% ammonium nitrate and at least 12% water of crystallization, is not subject to these Regulations". Provision 208 of the U.N. Orange book.

8. The following 2003 report suggests that sodium and potassium nitrate in its prilled form may not meet the UN (Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria, 3rd ed. United Nations, N.Y. 1999) definition of oxidizers. "Oxidizing Properties of Two Nitrate Compounds (NPP-TA) and (SSA-R)" Mak, W.A.; TNO report PML-2003 C129rev, October 2003

9. With following label: "Danger! Strong oxidizer. Contact with other material may cause fire. Causes irritation to skin, eyes and respiratory tract. Harmful if swallowed or inhaled".i.e. not security related. http://www.jtbaker.com/msds/englishhtml/C0451.htm (Oxidizing material. May catch fire in contact with combustible materials. Avoid contact with organic materials.)

10. Review of the Classification of magnesium nitrate hexahydrate by the Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of the Classification and Labelling of Chemicals. ST/SG/AC.10/C.3/2005/48, ST/SG/AC.10/C.3/56 and ST/SG/AC.10/C.3/56/add 1.

TABLE 4.2 Risk Factors and Assessment of Overall Potential for Use of Common Explosive Chemicals in Bomb Making (from reference 1)

Chemical	Risk Factor Availability and Accessibility	Ease of Use in Bomb Making		History of Prior Use ^b	Overall Potential for Use
Ammonium nitrate ^c	Hiah	High	High	High	High
Sodium chlorate	Medium	High	Medium	High	Medium
Urea ^{<u>d</u>}	High	Low	High	High	Medium
Nitric acid ^d	High	Very low	High	High	Medium
Potassium chlorate	Very low	High	High	Low	Medium
Potassium nitrate	Low	High	Low	Low	<mark>Low</mark>
Potassium	Very low	High	Low	Low	Low
perchlorate					
Hydrogen	Low	Medium	Low	Low	Low
peroxide ^{<u>d,e</u>}					
Calcium nitrate	<mark>Medium</mark>	<mark>High</mark>	<mark>Low</mark>	<mark>Very low</mark>	<mark>Low</mark>
<mark>mixtures^I</mark>					
Sodium	Low	Medium	High	Very low	Low
hypochlorite ^e					
Calcium carbide	Low	High	Medium	Very low	Low
Dinitrotoluene	Medium	High	Very low	Very low	Low
Nitrobenzene	Medium	Medium	Low	Low	Low
Nitroparaffins ^{c,g}	Very low	Medium	Very low	Low	Very low
Picric acid	Very low	High	Very low	Very low	Very low
Potassium	Very low	High	Very low	Very low	Very low
permanganate	., .				. <i>.</i> .
Sodium chlorite	Very low	High	Very low	Very low	Very low
Active halogen-type	e Low	Low	Very low	Very low	Very low
biocides ^c					. <i>.</i> .
Calcium	Low	High	Very low	Very low	Very low
hypochlorite					

^a Assessment of affordability based on costs of material from chemical supply houses (except for active halogen-type biocides, as indicated by footnote c).

^b As determined by the committee based on its experience and information provided by Richard Strobel, ATF, in a personal communication, September 11, 1997.

^c Available from garden, swimming pool, and racing supply outlets.

^d Precursor requiring chemical reaction for conversion to an explosive.

^e Typically available as aqueous solution.

^f Ca(NO₃)₂/NaNO₃/NH₄Cl/Calcium cyanamide.

^g Includes nitromethane.