Chemical Incident Analysis
Involving Storage of Fertilizer Product

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Abstract
A forensic engineering analysis of a chemical incident is presented that was classified as a self-sustaining decomposition (SSD) event, which occurred in a load of 10,000 tons of NK 21-00-21 fertilizer bulk stored inside a warehouse in the city of São Francisco do Sul in Brazil. The chemical reaction developed within the fertilizer mass and took several days to be controlled, resulting in the evacuation of thousands of residents. The water used to fight against the reaction, after having contact with the load of fertilizer material, promoted changes in adjacent water bodies, causing the death of animals (fish, crustaceans, and amphibians). The smoke from the chemical reaction products damaged the incident's surrounding vegetation. Large SSD events are rare, with an average worldwide frequency of one every three years. Therefore, in addition to presenting a case study of this type of phenomenon, the main objective of this work is to discuss the causes that led to SSD reaction at this event, evaluate its consequences, and motivate future studies. Fire and external heat sources — factors that usually trigger the SSD — were ruled out as determinant factors of this SSD event. Small-scale experiments carried out concluded that a combination of an acidic condition, the presence of catalytic substance, and the occurrence of the “caking” phenomenon acted as primary triggers of the chemical incident.

Keywords
Self-sustaining decomposition, fertilizer, ammonium nitrate, forensic engineering, exothermic reaction, self-heating

Introduction
The city of São Francisco do Sul has a population of approximately 47,500 inhabitants, the majority of which had to be evacuated due to a chemical incident and the release of toxic gases. The event aroused chaotic situations in the city, such as lack of fuels and supplies, various thefts, and environmental damage to the surrounding fauna and flora. Several public security agencies were involved in evacuating the population, fighting and controlling the chemical incident, as well as investigating its causes in order to provide forensic evidence to courts of law.

A multidisciplinary staff of forensic officers (engineers, chemists, and environmentalists) was nominated by the state government to register, collect, and analyze evidence as well as find the causes of the chemical incident and evaluate its consequences. The forensic officers’ investigations led to a hypothesis related to a self-sustaining decomposition (SSD) event that involved ammonium nitrate-based fertilizer. Published scientific studies show that events of this nature are most probably caused by an external heat source. However, there was no such evidence at the scene, making the forensic analysis a challenge.

Ammonium nitrate (NH₄NO₃) is a product that has two main commercial uses worldwide: one as a key ingredient for blasting agents or high explosives (e.g., manufacture of ANFO - Ammonium Nitrate/Fuel Oil); the other as a plant nutrient in the manufacture of ammonium nitrate-based fertilizers. Ammonium nitrate-based fertilizers in the widest sense refer to a variety of commercial products, roughly classified according to their application into two types: straight nitrogen fertilizers, where the element nitrogen is the principal plant nutrient; and compound (complex or blend) fertilizers, NPK/NP/NK products that contain at least one other nutrient, such as phosphate (P) or potash (K), in addition to nitrogen (N).

Hazardous Properties
All fertilizers based on ammonium nitrate, under normal conditions, are stable materials, which in themselves present no risk. However, under abnormal conditions, they...
can give rise to hazards, including intensification of pre-existing fires, self-heating, thermal decomposition (including self-sustaining decomposition), and, under extreme conditions, explosion.

**Fire Hazard**

Fertilizers based on ammonium nitrate are not combustible. Although not all ammonium nitrate-based fertilizers are classified as oxidizers, they are oxidizing in nature. When heated sufficiently, they can decompose, giving off oxygen or nitrogen oxides that can assist other materials to burn (even if air is excluded).

Experience shows that fires in fertilizer stores usually start outside the fertilizer stacks or heaps in combustible materials inappropriately stored near the fertilizer or in associated equipment, such as trucks or belt conveyors. Therefore, the risk of fire depends on other general combustible materials that may be stored together with the fertilizer (heated parts, flammable substances, or combustible materials).

**Self-Heating**

Self-heating is the phenomenon in which the temperature within a body of material rises due to the heat being generated by some process taking place within the material. Ammonium nitrate-based fertilizers are thermally stable and are not prone to self-heat in normal conditions of storage (i.e., without moisture absorption or presence of contaminants). However, when stored under abnormal conditions that result in an acidic mixture, they can produce a self-heating due to the exothermic chemical reactions between the fertilizer’s components. If the heat produced by these reactions has difficulty dispersing to the atmosphere, then it can lead to a thermal decomposition of the fertilizer with the release of gases that contain toxic compounds.

**Thermal Decomposition**

When heated above 210°C, ammonium nitrate-based fertilizers decompose and release toxic fumes. The decomposition gives off a mixture of gases, such as water vapor, nitrogen, nitrous oxide, nitric oxide, ammonia, chlorine, hydrogen chloride, and others gases, including oxide vapors of nitrous oxide (NO₂), and carbon (CO, CO₂), resulting from a series of reactions. Therefore, ammonium nitrate-based fertilizers will suffer decomposition if involved in a fire or exposed to external heat.

The thermal decomposition process is complex. First, decomposition develops endothermically; afterward, a complex set of exothermic reactions happens.

When these fertilizers are acidic and/or contain materials that have a catalytic effect, such as chlorides, copper, and/or zinc, thermal decomposition can take a different course — and be initiated when the fertilizers are in the solid state, and toxic oxides of nitrogen (together with hydrochloric acid vapor and chlorine gas) can be evolved. It is worth mentioning that it is important to look at the potential risk that compound fertilizers based on ammonium nitrate containing chloride in their composition might have (e.g., compounds with ammonium nitrate and potassium chloride), as extremely low chloride contents may be sufficient to produce a significant effect on thermal decomposition.

**Self-Sustaining Decomposition**

In many cases, the decomposition (initiated by an external heat source) will stop when the external source is removed. With some fertilizers, however, the decomposition will continue and spread deep within the mass of material — even when the heat source is removed. This is the phenomenon of self-sustaining decomposition, sometimes referred to as “cigar burning” or “fuse-type decomposition,” where the decomposition propagates through the mass of the material. No flames are produced unless paper, oil, or other organic material is present. The decomposing material does not usually get hot enough to glow. Fume off conditions are the most dangerous of situations due to the large mass being involved in such a short time.

In addition to external sources of heat, there are other factors that can trigger self-sustaining decomposition. Fertilizers based on ammonium nitrate under acidic conditions and/or containing materials that have catalytic effects, such as chlorides or copper, can also trigger it. Ammonium nitrate-based fertilizers whose formulation contains the presence of chloride (e.g., potassium chloride) have a greater susceptibility to self-sustaining decomposition.

Hadden, Jervis, and Rein report that incidents of self-sustaining decomposition can be initiated by self-heating if the heat generated by it cannot be lost to the surroundings at the rate greater than it is generated, thus providing a thermal runaway, which allows heat to accumulate in the mass of the fertilizer material. Hadden and Rein (qtd. in Babrauskas) highlight that this will occur when large quantities of fertilizer material remain undisturbed for long periods of time (e.g., in bulk storage.
or transportation), when the room temperature is high, and/or if there is contamination with organic material with which the ammonium nitrate begins to react directly at approximately 100°C.

According to Hadden and Rein10 (qtd. in Kiiski17), large self-sustaining decomposition events are rare with an average worldwide frequency of one every three years. For Kiiski8, the demand for more concentrated compound fertilizers from the 1950s led to a group of compound fertilizers whose concentration enabled emergence of the hazard of self-sustaining decomposition.

The incidents experienced in fertilizer warehouses and in maritime transport cargoes in the past motivated a number of studies on the factors that govern self-sustaining decomposition. In addition, international standards were developed for transportation and storage of fertilizers1,8,9,10.

**Explosion Hazard**

The risk of explosion of ammonium nitrate-based fertilizers from past major accidents is obviously a bigger threat in terms of the extent of immediate potential consequences. Indeed, a number of these tragedies have killed hundreds of people, injured many more, and led to massive destruction, as in Oppau (Germany, 1921), Texas City (United States, 1947), Brest (France, 1947)2,3, and recently in Beirut (Lebanon, 2020).

The high nitrogen content in the product was identified years ago as a key factor in the detonation ability. This is the reason why most current regulations and codes differentiate ammonium nitrate-based fertilizers according to the concentration of nitrogen content2,7.

The two main mechanisms that can potentially cause an explosion in an ammonium nitrate fertilizer heap are the development of rapid decomposition (deflagration) in a fire situation and the initiation by a shock produced by an adjacent high-energy explosion3. When heated strongly under confined conditions (in a fire, for example), ammonium nitrate-based fertilizers can decompose violently, causing an explosion2,6,11,14.

Currently, fertilizers based on ammonium nitrate are difficult to detonate, as such fertilizers are produced to have high resistance to detonation and thus require very energetic shocks. However, if fertilizers of these kinds are not treated properly, a number of factors can decrease this resistance, including prolonged heating, limited ventilation, presence of contaminants, strongly acidic conditions, particle size reduction, and thermal cycling2,3,6.

Contamination of fertilizer with combustible and other reactive substances increases this risk. The explosion hazard is increased by the presence of organic materials such as oil, sulfur, grease, charcoal, and combustible dusts near the fertilizer2,6,14.

**Thermal Cycling**

Among the crystalline transitions to which ammonium nitrate is subject, one of particular interest to the fertilizer industry is the transition to 32°C. This crystalline transition is accompanied by a substantial volume increase or decrease (approximately 3.6%) as the temperature is raised or lowered, respectively. Thus, temperature fluctuations across 32°C in storage situations of ammonium nitrate-based fertilizers produce effects of expansion, and contraction of the material volume can cause the product to break down into fine dust by thermal fatigue3,4,5,7. Therefore, physical disaggregation of the fertilizer can be promoted while stored in direct sunlight or under conditions where fluctuations between high and low temperatures can occur, particularly if they are inadequately stabilized or have picked up moisture. The transition at 32°C is particularly harmful in climates where ambient temperature is often close to this temperature3,4,5,7.

**Humidity**

Ammonium nitrate-based fertilizers, like many other fertilizers, are hygroscopic. Therefore, they tend to absorb moisture from the atmosphere to which they are exposed, depending on the relative humidity of the air. In general, unwanted moisture absorption causes product deterioration as caking and/or physical breakdown3,12.

Caking is the formation of a solid mass or lumps of fertilizer from individual particles. The amount of free water remaining in the fertilizer after manufacture or absorbed during storage has a huge impact on a fertilizer’s tendency to cake (form lumps)13. NK fertilizers are made from ammonium nitrate and potassium chloride, and are subject to hard caking. Breakdown can also occur in wet conditions. Under such conditions, the material may disintegrate into dust or wet powder7.

The more hygroscopic a fertilizer is, the more problems you can expect during storage and handling. The Critical Relative Humidity (CRH) is the property that is used as an indicator of the degree of likely interaction with atmospheric moisture. It is the value of the relative humidity of the surrounding air, above which the material
absorbs moisture and below which it does not\textsuperscript{3,7,12,13}. According to Clayton\textsuperscript{12} and Rutland\textsuperscript{13}, the CRH for commercial fertilizers compounds of ammonium nitrate and potassium chloride mixtures is between 55\% and 67.9\%.

**Contaminants**

Numerous incompatibilities have been identified with ammonium nitrate that may significantly increase the fire and explosion risk at both manufacturing and storage facilities — and lower the decomposition onset temperature in many cases. The determination of the sensitizing degree of the various potential contaminants (organics, chlorides, metals, metallic salts, urea, etc.) would also contribute to scientific analysis of the hazardous processes. However, due to its complexity (and despite the scientific interest aroused), the decomposition mechanisms influenced by contaminants are not yet defined\textsuperscript{1,2,11}.

Regarding ammonium nitrate-based fertilizers, as the solution becomes more acidic, its stability decreases, and it may be more likely to decompose and/or explode\textsuperscript{3,4,5,7}.

In cases where potassium chloride is part of the ammonium nitrate fertilizer mixture, consideration should be given to the possibility of self-sustaining decomposition and the overall level of the coating. Potassium chloride is the main potassium source in fertilizers; however, it is readily dissolved in water-forming chloride ions, which are catalysts of the thermal decomposition reaction\textsuperscript{3,4,5,6,7,8,9,10}.

**São Francisco do Sul**

**Self-Sustaining Decomposition Incident**

This case study refers to a chemical incident classified as a self-sustaining decomposition event that took place in 10,000 tons of NK type 21-00-21 fertilizer cargo stored in bulk form in a warehouse. The chemical incident, shown in Figure 1, took place in the city of São Francisco do Sul of Santa Catarina (SC) State in Brazil. The reaction developed inside the mass of fertilizer for several days until controlled, resulting in the evacuation of thousands of inhabitants.

**Forensic Exams**

Field and laboratory data were collected. The field examinations were divided into two parts: the environmental impact assessment and the warehouse analysis. There was substantial environmental impact on the surrounding vegetation and adjacent water bodies. At the warehouse, the layout patterns of reacted material in the structure and the morphological features of the reacted material allowed the identification of the origin of the reaction. Search, registration, and collection of traces that could be related to the incident were performed by the forensic team of six scientists and engineers. Virgin and reacted fertilizer material samples for the accomplishment of comparative forensic analyses in the laboratory were collected. Laboratory analyses included granulation and acidity exams. In addition, flammability and temperature tests were also performed (Figure 2).

**Environmental Impact**

The water used by the firefighters to suppress and control the chemical reaction, after contacting the load of fertilizer material, became contaminated with ions (NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{-}, K\textsuperscript{+} and Cl\textsuperscript{-}), and was absorbed by the adjacent soil and water bodies. Measurements of the surrounding water bodies’ conditions showed high values of acidity (low pH), salinity, and nitrogen in the form of ammonium (NH\textsubscript{4}\textsuperscript{+}) and nitrate (NO\textsubscript{3}\textsuperscript{-}) ions. The contaminated water promoted changes in the soil and adjacent water bodies and resulted in the death of animal species (fish, as shown in Figure 3, crustaceans in Figure 4, and amphibians in Figure 5). It was also established that the smoke from the products of the chemical reaction promoted damage to the vegetation around the incident area. The surrounding vegetation was composed of native (Atlantic Forest) and exotic species (Figure 6).

<table>
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<tr>
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</tbody>
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**Figure 1**

Chemical incident (second day).

*Courtesy of the City Hall of São Francisco do Sul\textsuperscript{18}.*

**Figure 2**

Measurements at 450 m from origin on September 26, 2013.
**The Warehouse**

The warehouse that stored the fertilizer load had damages produced by the firefighters’ combat in order to extinguish the reaction of the incident. The chemical reaction’s origin occurred in the right posterior portion of the warehouse. It was identified by the presence of reaction by-products on the exterior face of the building wall (Figure 7) as well as by the intensified state of corrosion of metallic parts in this region, as a result of the oxidizing gases actions produced by the chemical reaction (Figure 8).

The fertilizer material stored in the warehouse had several macroscopic aspects, varying among solidified formations of alveolar-like deposits of the substance in the unchanged conformation (Figure 9). These characteristics were similar to those observed by Hadden and Rein\(^10\) in small-scale experiments with a diverse fertilizer composition and using a heat source (Figure 10).

Based on the EFMA manual\(^3\), the levels of ammonium nitrate and potassium chloride in fertilizers of type NK 21-00-21 were calculated, obtaining, respectively, 60% and

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**Figure 3**
Dead fish in the surrounding water bodies.

**Figure 4**
Dead crustacean in the surrounding mangrove area.

**Figure 5**
Dead amphibian in the surrounding water bodies.

**Figure 6**
Vegetation damaged: north (red ellipse) and northeast (yellow ellipse) of the warehouse.

**Figure 7**
By-products of the reaction on the outer face of the warehouse wall.
40%. According to experimental data from FM Global\textsuperscript{6}, this type of fertilizer will undergo self-sustaining decomposition (Figure 11).

Despite being the most common cause of thermal decomposition, the hypothesis of the incident having started by an external source of heat was ruled out. Besides the absence of traces of charring, there was no evidence of the presence of combustible materials (wood, straw, hay, gasoline, etc.), flammable substances, heated parts, or electrical equipment near the reaction’s origin area that might start a fire close to the fertilizer and trigger the chemical reaction by heat transfer. The analysis of the electrical system and the certification of their protective circuit breakers also did not corroborate the occurrence of an electrical fault or defect to support such a hypothesis.

It was not possible to state the storage conditions of the material prior to the chemical incident (height of the fertilizer material stack, distance from the walls, presence of contaminants, etc.) due to the necessary actions of the firefighters to combat the incident. However, there was a load of 4,000 tons of the same batch of fertilizers from the same ship stored in the warehouse of another company in the same city about four kilometers away from the origin area. This material was analyzed because it was the same type fertilizer, transported in the same ship, stored nearby under similar ambient conditions, and was caked (Figure 12). Caking results with some bulk materials when it absorbs moisture.

The city’s closest weather station’s meteorological data reported an average of 82% of the relative humidity between the beginning of the fertilizer material’s storage (August 30, 2013) and the date of the incident (September 16, 2013).
Flammability Tests
Samples of virgin fertilizer material were subjected to flammability tests with a flame source, flammable fuel source (ethanol) associated with the flame, and an electric current source. Exposure to the flame (about 30 seconds of exposure with a flame height of 20 mm) did not lead to ignition, but to a thermal decomposition of the material that stopped whenever the flame source was removed. Applying absolute (99% to 100%) ethanol on the fertilizer associated with a flame reached the same result — no ignition. The thermal decomposition remained as long as there was ethanol to burn, and stopped when it finished. Electric current sparks applied on the fertilizer also did not produce ignition of the fertilizer. The samples are self-extinguishing materials after the source is removed (i.e., doesn’t support the fire).

Granulation, Acidity, and Temperature Tests
The virgin fertilizer material presented granulation characteristics in the form of spheres, which were brittle and easily sprayed powder when handled by applying small pressure with the fingers.

To evaluate the behavior of the substance in acidic medium, aliquots of 5g of fertilizer material were used in both granulated and pulverized form (eight samples for each granulated and pulverized form). These samples were tested with and without addition of acidic substance. In those tested in acid medium (four samples for each granulated and pulverized form), 1 ml of 5M hydrochloric acid was added. The samples were submitted to increasing temperature in the range of 30°C to 265°C in a programmable electric oven with timer drying control.

It was observed that the samples submitted to acidic medium developed yellowish coloration with temperature above 50°C and evolved to pink-whitish after 150°C when the material acquired an alveolar appearance similar to that observed at the event origin (Figure 13). Non-acidified samples retained the original (orange) coloration until the temperature of 210°C, when they evolved to pink-whitish and alveolar appearance. No significant differences were observed between the results obtained with the samples of granulated and pulverized material.

The results show that in an acidic medium, the decomposition reaction is catalyzed by the presence of chloride ions, according to Kiiski7,8 and with Hadden and Rein10, which demonstrate that the chloride catalyzed decomposition reaction is the main mechanism involved in self-sustaining decomposition.

External Heat Source
In the adjacent area to the storage of the fertilizer material, there was no presence of combustible materials or flammable substances (wood, gasoline, oils, grease, etc.) — neither of heated parts nor electrical equipment as well as no trace of carbonization. The warehouse where the fertilizer was stored had overhead electrical wiring that did not have any traces of electrical failure. During the combat to the chemical reaction, the firefighters reported no detection of flames. Thus, fire or external heat sources as the cause of the thermal decomposition were ruled out.

Physical Breakdown
Temperature fluctuations above and below 32°C were common during the days and nights in the subtropical climate region of the incident site. This caused successive crystalline transitions and its effects of expansion and contraction of the material volume, which, as well as the verified moisture absorption, facilitated product breakdown into fine dust. In the form of dust, the contact
surface of the material is higher — the higher surface area of the reagents, the higher the rate of a reaction.

Caking
The moisture absorption also promoted the “caking” phenomenon. The hardening of the outer layer of the fertilizer pile imprisoned air among the fertilizers’ pellets, acting as a thermal insulation (hampering the heat exchange between the interior of the heap and the environment).

Dissociation of Salts, Acid Mixture, and Catalyzer
The fertilizer compound (NK 21-00-21) was a mixture of two salts: ammonium nitrate \((\text{NH}_4\text{NO}_3)\) and potassium chloride \((\text{KCl})\). The absorption of moisture (water) by these salts led to the dissociation of salts into ions \((\text{NH}_4^+, \text{NO}_3^-, \text{K}^+, \text{Cl}^-)\) generating an acidic mixture (low pH). Additionally, the chloride ion \((\text{Cl}^-)\) generated in the dissociation consists of a catalyst for the thermal decomposition reaction. The exams performed showed that the samples of the material, in an acid medium, developed thermal decomposition reactions (yellowish color) with temperatures around 50°C.

Conclusions
Based upon the scene examination, laboratory tests/analysis, and reviewed literature, the hypothesis that an external heat source (mechanical, electrical, fire) caused the self-sustaining decomposition was eliminated.

The most probable cause was the combination of the known air thermal cycling, the observed moisture absorption, as well as the influence of chloride ions on the acid medium. This hypothesis was supported and validated by:

a. The physical breakdown of the fertilizer promoted by thermal cycling, which, together with the absorption of moisture (water), becomes susceptible to the dissociation of salts of potassium chloride \((\text{KCl})\) from its own composition, forming chloride ions;

b. The fertilizer, in the presence of moisture (water), starts to present acidic conditions;

c. The acidic condition associated with the presence of chloride and/or other contaminants are characteristics that lead to a self-heating reaction; and

d. The long period that the material remained inert, combined with the low thermal conductivity of the fertilizer, aggravated by the caking phenomenon that formed a thermally insulating layer. This caking made it difficult to dissipate the heat generated inside the fertilizer pile to the environment. Considering that the heat generated by the chemical reaction was greater than that dissipated to the environment, the consequent evolution to a chloride \((\text{Cl}^-)\) catalyzed thermal decomposition reaction — and, afterward, to a situation of self-sustaining decomposition — is the most probable cause.

The rarity of self-sustaining decomposition events — especially those that are not triggered by the action of external heat sources — require further studies on the subject.

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